NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

FINAL PROJECT REPORT
NSF FORM 98A

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PART I–PROJECT IDENTIFICATION INFORMATION

1. Institution and Address	2. NSF Program	3. NSF Award Number
Georgia Institute of Technology 225 N. Avenue, N. W. Atlanta, Georgia 30332	Solid State Chemistry	77-04110
	4. Award Period From 8/1/77 To 7/31/80	5. Cumulative Award Amount $54,000

6. Project Title

Collision Induced Optical Spectra of Solids.

PART II–SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

The objective of the project is to understand the inelastic processes whereby fast projectiles transfer their energy to a solid target and how such mechanisms are related to the chemical nature of the surface.

Ions (generally H^+, He^+, Ar^+ or Kr^+) from an accelerator (5 to 200 keV) are incident on solid targets and an examination made of the optical and electron emission spectra.

The formation of inner electron shell vacancies in these events is due to curve crossing in the transient molecule AB formed by the moving projectile A and the stationary target atom B. Moreover we have shown decisively that the excited particles are ejected (sputtered) from the surface and undergo decay with electron ejection (by the Auger process) in free space. Oxidation of the target atters only the probability of excited state formation; not the nature of the excitation nor of the decay mechanisms.

Light emission from the beam impact point represents formation of atoms (or ions) with excited outer electron shells. We have shown that impact of monoatomic nitrogen ions on silicon gives rise to a molecular nitrogen spectrum from ejected molecules. There is a high degree of rotational and vibrational excitation suggesting that two atoms eject simultaneously and associate in free space.

PART III–TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

1. ITEM *(Check appropriate blocks)*	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses	✓				
b. Publication Citations		✓			
c. Data on Scientific Collaborators		✓			
d. Information on Inventions	✓				
e. Technical Description of Project and Results		✓			
f. Other *(specify)*					

2. Principal Investigator/Project Director Name *(Typed)*	3. Principal Investigator/Project Director Signature	4. Date
Edward. W. Thomas		10/3/80

NSF Form 98A (5-78) Supersedes All Previous Editions

GEORGIA INSTITUTE OF TECHNOLOGY

ATLANTA, GEORGIA 30332
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SCHOOL OF PHYSICS

1 October 1980

MEMORANDUM

TO: National Science Foundation
Division of Materials Research
Washington D.C. 20550

Attn: Dr. Fred E. Stafford
Program Director
Solid State Chemistry Program

FROM: Georgia Institute of Technology
Atlanta, GA 30332
Principal Investigator: Professor Edward W. Thomas

JUBJECT: Grant No: DMR 77-04110
Starting Date: 8/1/77; completion date: 7/31/80
Grant Title: Collision Induced Optical Spectra of Solids.

ITEM: Final Technical Letter Report.

I. Scientific Description of Research and Results.

The program was designed to study optical emission induced by energetic (5 to 200 keV) ion impact on solids. A mass analyzed ion beam was directed onto a target and optical emissions from the point of beam impact measured spectroscopically. An Auger electron spectrometer monitors the condition of the surface. By adsorbing various gasses onto the surface we can alter surface composition; changes to relative intensities of features in the optical emission spectrum provide a measure of the rate of an ion induced chemical change. During the work we found that the ion beam induced a copious Auger electron signal with distinct identifiable features. The literature discloses a number of previous studies of ion induced Auger spectra but there is confusion as to the nature of the excitation process and as to the location of the excited species when decay occurs. Since the objective of the research is to understand collisional energy transfer resulting in excited state formation it seemed appropriate to pursue studies of both inner shell processes (leading to Auger electron emission) as well as outer shell excitation mechanisms (leading to photon emission).

(a) Excitation of Inner Shells - Auger Spectra

Excitation of inner shells in collisions of heavy particles (e.g. Ne^+, Ar^+, Kr^+) with solid targets results from curve crossings in the transient molecular state AB composed of the moving projectile A and the stationary target atom B; this phenomenon[1] is well known in fundamental studies of bi-particle collisions in gas phase targets. The electron energy levels of AB vary as the internuclear separation first decreases on approach and then increases as A and B separate.

If two levels become degenerate an electron can transfer from one level to a vacant state in the other. As the atoms recede one is left with an inner shell vacancy that will subsequently be filled by an Auger decay giving rise to an electron of discrete energy. In general the promotion process creates vacancies in the 2p shell of the partner of lower Z^1. We have studied Auger spectra induced by 5 to 200 keV Ar^+, and Kr^+ impact on Aℓ, Si, Mn, Cr, Fe and Co which confirm the expected features of the process. A major question, and one for which the literature exhibits various conflicting answers is whether the final Auger event occurs for a particle in the target matrix (and therefore having the characteristics of a solid state transition) or whether it occurs for target and projectile species ejected from the surface and into free space (having therefore the characteristics of a transition in an isolated atom or ion).

Extensive studies of the aluminum Auger spectrum induced by Ar^+ impact on Aℓ leads us to conclude that the most of the excited Aℓ is sputtered from the target as a neutral atom (with an inner shell vacancy) and decay occurs in free space giving the Auger spectrum of neutral Aℓ. This is different from conventional studies of aluminum Auger spectra where an electron is removed from an inner shell of an aluminum atom leading to an excited ion and the consequent emission of the ionized aluminum spectrum. There are similar conclusions for the excitation of Si by Ar^+ impact. Alteration to the chemical composition of the surface (forming oxides, nitrides, carbides etc.) changes the relative intensity of the spectral features but does not alter the basic line positions. The material has been largely published (see items 1,2 and 3 under publications and copies submitted with this document).

Studies of Auger spectra induced by Ar^+ on higher Z targets (Mn, Cr, Fe and Mo) show spectra that are predominantly from the projectile Ar with Doppler shifts and broadening indicating that the source is back scattered (rather than implanted) particles. There are also indications of interatomic transitions where a vacancy formed in a projectile is filled by electrons from a target atom. The identification of interatomic transitions is at best tentative and requires detailed confirmation. These studies have been published in items 1,2 and 4 of the publication list and are attached to the present document.

The equipment used in the studies to date has been a commercial CMA with a broad acceptance geometry that leads to substantial instrumental line broadening due to Doppler shifts from the moving excited species. A new analyzer has been built with a uni-directional collection geometry that will also provide an improved resolution. In the continuation of the work we propose to confirm our identification of the excited species and provide high resolution spectra of neutral atom Auger spectra which are not accessible in other types of excitation mechanisms. We intend also to study the apparent sensitivity of the excitation probability to the chemical state of the surface.

(b) Excitation of Outer Shells - Optical Spectra.

When a line optical spectrum is observed from the point of beam impact on the surface there is little doubt that one is observing atoms or ions decaying

in free space; in this respect the optical spectra are easier to interpret than the Auger emissions. A difference, however, is that there is little understanding of the mechanism of excitation. A model proposed by Andersen and Hinthorne[2] (to explain secondary ion spectra) is sometimes invoked to describe excitation. It suggests that there is a local high temperature plasma formed at the point of projectile impact and relative excitation probabilities are given by excitation rates applicable to a plasma in Local Thermodynamic Equilibrium. Although relative line intensities do sometimes follow the LTE model there is in fact no physical basis for invoking the idea of a plasma. Moreover the model in no way explains why the intensity of atomic lines changes substantially when the chemical nature of the target is altered (e.g. two orders of magnitude increase in intensity of aluminum lines in going from Aℓ to oxidised aluminum).

In a limited number of situations one observes, from the target, emission of molecular lines. There are our own observations of transition metal oxide molecular emissions[3], CN molecules on alkali halides[4] and N_2 spectra due to[5] bombardment of Si with N^+. These offer an interesting probe of excitation and ejection processes. The state of electronic excitation is related to the inelastic energy loss processes of the projectile. The states of vibration and rotation are related to the relative motion of the atoms at the time the molecule is formed.

We have devoted much time and effort to a renewed study of the formation of CN on alkali halides discovered by us[4] in 1976. This occurs when a crystal carrying adsorbed CO, N_2 and H_2O is bombarded by He^+ or H^+. The intention was to relate the CN intensity (measured by the optical emission) to the surface density of C,N and O (measured by conventional Auger spectroscopy). The experiment has had only limited success. In part this is because the CN emission occurs for surface coverages of C,N and O that lie at, or below, the detectability limits of the Auger spectrometer (i.e. less than 1% of a monolayer). We find this quite surprising. Indeed it proves very difficult to induce absorption of measureable C, N and O concentrations at all, except on highly damaged crystals. The matter continues to be studied.

We have recently started to study the N_2 emission spectra occuring when N^+ bombards Si. Here the emisssion intensity builds up with dose suggesting that the excited N_2 is previously implanted N that is sputtered from the surface. There are indications that the N_2 has a very high degree of rotational and vibrational excitation suggesting that two N atoms are sputtered separately but simultaneously and associate into molecular N_2 alter leaving the surface.

(c) Conclusion

The objective of the research is to come to some comprehensive understanding of the energy loss processes that lead to excitation of target species and how this is related to the chemical nature of the target matrix. We have made extensive studies of Auger spectra which show that excitation results from curve crossing in a transient molecular complex. The relative likelihood of certain decay channels seems dependent on the chemical nature of the target prompting us to speculate that

the ejected species may in fact be a molecule, the nature of which varies with the chemistry of the target. The optical spectra show directly that molecules are in some cases ejected, frequently with high rotational and vibrational excitation. Quantitative comparisons between Auger and optical spectral signals suggests that in many cases an atom is ejected with an inner shell vacancy and subsequent Auger decay leaves an ion with excited outer shells; this then undergoes radiative decay leading to observed photons. We are continuing to pursue the possible correlations between these two types of spectra.

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5. Unpublished work. Similar preliminary observations were reported by R. S. Bhattacharya et. al., Rad. Effects 33, 57 (1977).

II. Publications.

"Ion Induced Auger Spectroscopy", E. W. Thomas, K. O. Legg and W. A. Metz, Nucl. Instr. Meth. 168, 379 (1980).

"Auger Spectra Induced by Ion Impact on Metals", K. O. Legg, W. A. Metz and E. W. Thomas, Nucl. Instr. and Methods 170, 561 (1980).

"The Auger Spectra Induced by 100 keV Ar^+ Impact on Be, Aℓ and Si", W. A. Metz, K. O. Legg and E. W. Thomas, J. Appl. Phys. 51, 2888 (1980).

"Identification of Auger Spectra Induced by Ar^+ and Kr^+ Impact on Transition Metals", K. O. Legg, W. A. Metz and E. W. Thomas, J. Appl. Phys. 51, 4437 (1980).

"Formation of Excited States by Ion Impact on Surfaces", Progress in Surface Science (accepted for publication). (A comprehensive review of some 200 pages in length including a complete bibliography on inner and outer shell excitation processes.)

III. Theses.

None (One is being written at the present time).

IV. Scientific Collaborators.

Werner A. Metz. Graduate student working on all phases of the project and writing a Ph.D thesis on this work.

Leo Efstathiou. Graduate student (Ph.D. program) started 6.1.80.

Ray Whaley. Graduate student (Ph.D. program) started 9.1.79 (On special fellowship, no cost to project).

Keith O. Legg, Research Scientist, worked on the Auger studies in an advisory capacity supported by funds from the state of Georgia.

V. Comments.

(a) The project supported by this grant has been renewed as DMR-8000671, to continue study of Optical and Auger spectra.

(b) Reprints of publications 1,2,3 and 4 are attached. An abstract of publication 5 is attached, reprints will be transmitted after publication (scheduled for early 1981).

(c) In publications 1,2 and 3 above we acknowledged not only NSF support but also partial support from D.O.E. This was done because W. A. Metz (the student) was supported by NSF, K. O. Legg (Research Scientist) was supported by D.O.E. and E. W. Thomas (Principal Investigator) obtained support from both sources. This confused situation arose because the work (on ion-induced Auger spectra) was not originally a component of the program proposed to DOE nor that proposed to NSF but arose as a by-product of work on both programs. We admit that the form of acknowledgement was not in accordance with NSF guidelines. This will not occur again as the Auger spectroscopy is included only under the continued NSF support. Publications 4 and 5 acknowledge only NSF support since during that work two authors received support from only NSF and the third (K.O.L.) was supported by Institutional resources.

Respectfully submitted

Edward W. Thomas
Professor of Physics
Principal Investigator

EWT/rh

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ION INDUCED AUGER SPECTROSCOPY

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Auger electron spectra are induced by impact of heavy ions (e.g. Ar^+) on surfaces; it has been suggested that analysis of such spectra would be a useful technique for surface analysis. We have examined the Auger spectra for various projectile–target combinations and present as representative data the spectra for 100 keV Ar^+ impact on Al, Cr, Mn, Fe and Co. For a projectile incident on a species of higher nuclear charge the spectrum is dominated by Auger lines from the projectile, broadened considerably by the Doppler effect due to the projectile's motion. The spectra are not characteristic of the target and therefore offer no opportunity for surface analysis. For a projectile incident on a target of lower nuclear charge the spectrum is that of the target species but the spectrum is consistent with the source being sputtered excited atoms; the Auger electrons do not come from the surface. We conclude that the ion induced Auger spectra are in general not a convenient method for surface analysis.

1. Introduction

Auger electron spectra induced by electron impact provide an accepted technique for analysing the composition of a surface. Auger electron spectra are also induced by ion impact on a surface. It has been suggested[1]) that surface analysis might conveniently be performed by recording the ion induced Auger spectrum. The purpose of this paper is to examine this suggestion. We present various Auger spectra induced by ion impact, discuss the nature and origin of the ion-induced Auger electron spectrum and conclude that the exitation process is far more complex than for electron induced Augers.

The experimental arrangement employs a conventional Varian Auger electron spectrometer using a cylindrical mirror analyser (CMA) to analyse electrons ejected from metal targets in a uhv environment. The incident ion beam was produced by an Ion Implanter capable of operation from 30 to 200 keV. The angle of ion beam incidence was approximately 60° to the sample surface normal; the CMA axis was at 35° to the surface normal and therefore at 95° to the incident ion beam. Samples were prepared by mechanical polishing and electropolishing. Further in-situ cleaning was possible by sputtering using either 100 keV Ar^+ ions from the accelerator or 3 keV Ar^+ ions from a separate ion gun. Auger electron spectra were produced using energetic ions from the ion implanter; for comparison purposes we could also produce electron induced spectra using the integral electron gun fitted co-axially in the Varian CMA analyser. Spectra were recorded in either the derivative mode (using a 5 eV modulation of the CMA voltage) or in the integral mode by pulse counting using a multichannel analyser (and with no spectrometer modulation). In general we preferred to use the integral mode of operation since this provides the true shape of the Auger spectra lines. However for the low energy LMM lines of heavy metals the Auger peaks are superimposed on a very intense secondary electron background; in such situations the derivative mode of operation was necessary in order to establish the existence and energy of a peak.

2. Results

We shall consider first the spectra induced by Ar^+ impact on aluminium. The spectrum is dominated by Auger lines from the target as are the spectra for other targets (e.g. Be and Si) whose nuclear charge is less than that of the projectile. Fig. 1 shows integral spectra and fig. 2 derivative spectra. The integral spectrum for electron impact (fig. 1a) and that for ion impact (fig. 1b) are similar in that they are dominated by a line at 67 or 61 eV which one may confidently ascribe to the filling of an L-shell vacancy[2]). There are however significant differences in detail. The electron induced spectrum shows a tail towards lower energy which is related to energy loss by the electrons as they traverse the distance from the point of excitation to the surface; electrons excited below the surface are observed at lower energies than those excited at the surface. No such "loss tail" is seen on the ion induced spectrum. Analysis of the derivative spectrum taken with electron impact (fig. 2a) shows subsidiary peaks at 15 eV and 27 eV below the main peak which are consistent with Auger electrons emerging

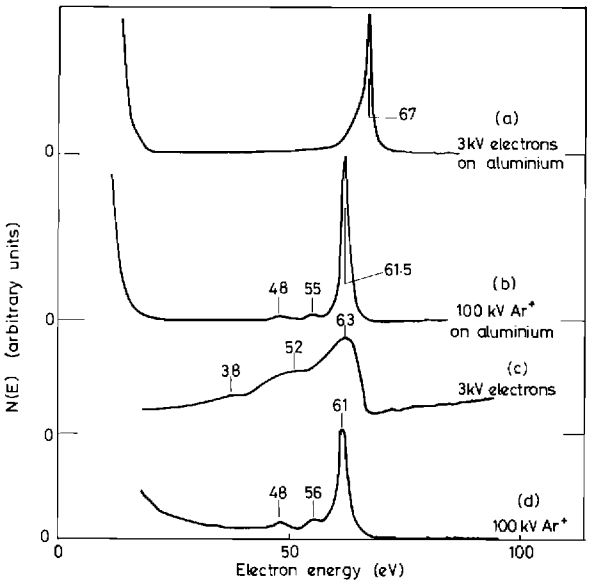

Fig. 1. Auger electron spectra taken in the integral mode. (a) 3 kV electrons on aluminium; (b) 100 kV Ar^+ ions on aluminium, (c) 3 kV electrons on oxidised aluminium; (d) 100 kV Ar^+ ions on oxidised aluminium.

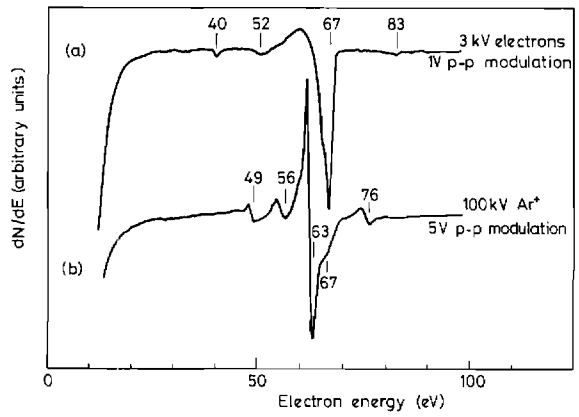

Fig. 2. Auger spectra taken in the derivative mode, (a) 3 kV electrons on aluminium; (b) 100 kV Ar^+ ions on aluminium.

after having excited bulk and surface plasmons[3]). The ion induced spectrum also shows subsidiary peaks (at 48 and 55 eV on the integral spectra) but their position is not consistent with plasmon excitation. In spectrum 1c we show the spectra observed under electron impact for an oxidised surface; the whole spectrum is changed. The electron induced Auger electron is emitted by filling of an L-shell vacancy by an electron from the valence band with the simultaneous ejection of a second valence band electron. The oxide has a different valence band structure from the metal and consequently exhibits this different Auger spectrum. No such change is seen in the ion-induced spectrum (spectrum d) when the surface is oxidised. Thus the ion induced spectra show none of the characteristics expected for the exicted atom being in the solid matrix of the metal; there is no loss tail, no plasmon structure and no matrix effect (as when the oxide is formed). One must conclude that the source of ion induced Auger electrons is not located in the solid.

It is also to be noted that there is a major difference between the energy of the major peak in figs. 1a and 1b; for ion impact it lies 5.5 eV lower than for electron impact. It has sometimes been argued that the width of the ion induced aluminium line is less than that of the electron induced line[4]); this was based on analysis of derivative spectra such as those shown in fig 2. This conclusion is misleading. The integral spectra show that much of the width of the electron induced line is caused by the loss tail. If we discount the loss tail then the electron induced line is about 1.4 eV fwhm while the ion induced line is wider at about 2.3 eV fwhm. It is well known that there is a substantial difference between the nature of the electron and ion impact excitation mechanisms. Electron impact forms an L-shell hole by direct Coulomb excitation. For 100 keV Ar^+ ion impact Coulomb excitation is expected to be small and core hole formation occurs primarily by an electron promotion mechanism during the temporary formation of an Ar^+ + Al molecular system. The mechanism is well discussed by Louchet et al[5]) and is described in a fundamental manner by Barat and Lichten[6]). For the case of Ar^+ on Al the vacancy formation is by promotion of a 2p electron forming an L_{II} or L_{III} hole; promotion does not occur in the inner shells of the argon ion and hence no argon Auger spectrum is seen. Promotion may also occur by Al+Al collisions in the collision cascade; again this will cause L_{II} and L_{III} vacancies of the Al system[6]). It is not clear whether promotion occurs primarily by the Ar^++Al event or by the Al+Al collision cascade. Benazeth et al.[7]) show theoretically that the symmetrical Al+Al collisions will produce a negligible fraction of the L-shell vacancies; on the other hand Vrakking and Kroes[8]) show that the Al spectrum is also produced by Ne^+ impact and here the promotion in the Ne^++Al collision will occur in the 2p shell of the neon and the only source of 2p vacancies in Al must be the symmetric Al+Al collisions. In any case whether the excitation occurs in Ar^++Al or Al+Al, the collision is violent, involv-

ing energy transfer to the Al atoms of at least 300 eV[8]). Taking the product of recoil speed for 300 eV Al atoms and the theoretical lifetime of the 2p vacancy[9]), the decay length for the recoiling Al atoms with 2p vacancies will be 61 Å. By contrast the depth from which 61 eV electrons can escape out of Al is only 4.2 Å[10]). Thus atoms recoiling into the solid will in general emit their Auger electrons at a depth from which the electrons cannot escape. It follows that only excited Al atoms ejected out of the solid (i.e. sputtered) will emit Auger electrons that can be detected. This is consistent with our discussion of line shape which also implies that the Auger spectrum is from ejected particles. If the emerging Al atoms have energies of around 300 eV then the detected line will be Doppler broadened by up to 2.5 eV; this is consistent with the width of the observed lines.

Auger spectra of aluminum induced by gas-phase bi-particle $Ar+Al^+$ collisions show eight or more lines identified as being from ionized states of aluminum[11]). The spectra of the present experiment are much simpler and we are led to examine whether they might be from neutral aluminum. An Al atom with a single 2p vacancy (i.e. $2p^5 3s^2 3p^2$ configuration) decaying to the $2p^6 3s 3p$ or $2p^6 3p^2$ states of Al^+ will produce Auger electrons of energy (estimated from the theoretical binding energies of Shirley et al.[12]), 64 and 57 eV. It is known that Auger electron energies predicted in this way may be too high by as much as 4 eV in some cases[12]). Thus we would argue that the peaks predicted at 64 and 57 eV could be those which are observed at 61.5 and 55 eV. Decay of an Al^+ ions of a $2p^5 3s^2 3p$ configuration to a $2p^6 3s$ or $2p^6 3p$ state will produce electrons at respectively 56 and 49 eV coinciding exactly with the two observed subsidiary peaks. The peak seen at 76 eV in the derivative spectrum has already been identified by Viel et al.[14]) as due to ejected atoms with two 2p vacancies.

Recently Vrakking et al.[8]) have claimed that the ion induced spectrum of Al is from Al atoms deep inside the solid within the disturbed region created by the collision cascade. If this were the case then the emerging electrons would have a very high probability of ionizing other atoms in the cascade and losing an energy equal to the relevant ionization potential. Indeed since ionization cross sections are typically[14]) 10^{-16} cm^2 the probability for such events should be almost unity for all electrons except those from the outermost layer of the surface. Thus we would expect a peak from aluminum 5.98 eV below the main structure; we observe the first subsidiary peak 6.5 eV below the main structure. Furthermore, when the surface is oxidized we should observe an additional peak with a 13.6 eV loss due to ionization of oxygen. While there is a peak at almost this energy it is present when the aluminum is clean and does not increase on oxidation. We conclude that there is no evidence for the electrons coming from Al atoms in a disturbed collision cascade region.

We have also examined the Auger spectra induced by Ar^+ ion impact on various heavy targets; as representative examples we show in fig. 3 spectra induced by 100 keV Ar^+ impact on Cr, Mn, Fe and Co. The spectra are shown only in derivative form; as a result of the large secondary electron background the Auger peaks are not displayed clearly in the integral mode of operation. The spectra are complicated and bear no close resemblance to the well known electron induced spectra of these elements. Hole formation by electron promotion mechanisms for these cases where the target nuclear charge exceeds that of the projectile will lead[6]) to hole formation in the L_{II}, L_{III} shells of the argon

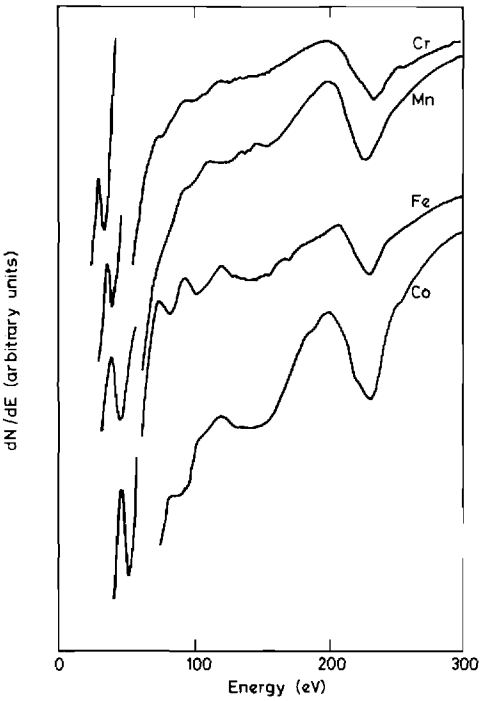

Fig. 3. Auger spectra taken in the derivative mode for 100 kV Ar^+ ions incident on Cr, Mn, Fe and Co. Note that the break in the curves at around 60 eV occurs when the sensitivity was reduced to accommodate the full spectrum on the plotter.

projectile. The broad peak between 210 and 260 eV is indeed the LMM line of Ar. The considerable breadth is consistent with a Doppler broadening effect[16]) due to the source of the electrons (the argon projectile) being in motion when decay occurs. Indeed detailed analysis of line width suggests that the argon Auger electrons arise primarily from backscattered projectiles which have emerged from the target. A variety of additional structure is seen at energies from 80 to 200 eV. We have tentatively ascribed this to LMM transitions involving a vacancy in the $L_{II,III}$ shell of Ar with the decaying and ejected electrons arising from metal atoms in the target; thus these lines are due to decay of an Ar–metal molecular complex. We do also observe the LMM peak of the metal in all cases lying in the region 40–60 eV. According to the electron promotion model[6]) excitation of the metal should not occur by argon–metal collisions; excitation of the metal is probably due to interaction of a recoiling metal atom with a second atom in the matrix. Whatever the precise origin of the structure in these spectra it is clear that the Auger spectra for these cases are dominated by features from the projectile and are not characteristic of the target.

3. Conclusion

The ion-induced Auger spectra fall into two groups which are characterized by the cases displayed here. Excitation is by an electron promotion mechanism following the general scheme detailed by Barat and Lichten[6]). For targets of nuclear charge greater than that of the projectile, hole formation occurs primarily in the projectile leading to a complex spectrum of lines broadened by the Doppler effect. Since such spectra are characteristic of the projectile (rather than the target) they are of little value for the analysis of the target material. For targets of nuclear charge less than that of the projectile the hole formation occurs in the target leading to a spectrum characteristic of the target. All evidence points to the observed Auger spectra being emitted from isolated atoms after their ejection from the solid.The states are complicated involving not only core vacancies but also excited outer electrons. Unlike electron induced Auger spectroscopy the ion induced process provides no information on band structure in the surface and spectra are not influenced by changes to surface chemistry. Ion-induced Auger spectra provide information similar to that of the SIMS technique since they are both related to ejection of atoms; there is little correspondence to the technique of electron induced Auger spectroscopy. We are forced to the general conclusion that ion induced Auger electron spectroscopy offers no general advantages over conventional electron induced Auger spectroscopy or SIMS.

This work was supported in part by the Magnetic Fusion Energy programme of DOE and in part by the Solid State Chemistry programme of the NSF.

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Nuclear Instruments and Methods 170 (1980) 561–564

AUGER SPECTRA INDUCED BY ION IMPACT ON METALS

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The Auger electron spectra induced by 20–200 keV Ar^+ ion impact on Al and Fe are examined and the spectral lines identified. For Al the spectrum is due to sputtered Al and Al^+ with one or two vacancies in the 2p shell. For Fe there are Doppler broadened lines from Ar plus subsidiary structure from interatomic transitions.

1. Introduction

Heavy ion impact on metal targets induces an intense emission of Auger electrons. The excitation mechanism is understood in terms of the electron promotion model of Barat and Lichten [1], involving the formation of a quasi–molecule AB from the interaction of a projectile A with an atom of the target B. The electron energy levels of the two particles are perturbed as they approach one another, allowing levels from one atom to become degenerate with levels of the second atom. This permits electron promotion from a filled inner shell on one atom to an unfilled shell on either atom, creating an inner shell hole which can subsequently decay by an Auger process. We have studied the Auger spectra induced by heavy ion impact on metals. Taking as examples the cases of Ar^+ on Al and Ar^+ on Fe which are studied most closely in this paper, the simple promotion model would suggest that Ar^+ on Al will result in 2p vacancies of Al while Ar^+ on Fe will result in 2p vacancies of the projectile Ar. It is also possible that the collision cascade resulting from the projectile impact will cause symmetric collisions Al + Al and Fe + Fe with sufficient energy to permit electron promotions; in this case there will be vacancy production in the 2p level of the target species.

We have performed a study of the Auger spectra induced by 20–200 keV Ar^+ and Kr^+ impact on Be, Al, Si, Cr, Mn, Fe, and Co. Due to space limitations this report will be restricted to discussion of Ar^+ + Al and Ar^+ + Fe which respectively represent cases where the vacancy production should occur in the 2p shell of the target (Ar^+ + Al) and the 2p shell of the projectile (Ar^+ + Fe). Details of the other cases will be presented elsewhere [2].

The experimental arrangement consisted of an ultra high vacuum chamber capable of base pressures below 10^{-10} Torr linked via a differentially pumped beam line to a 20–200 keV ion implantation accelerator. A standard commercial cylindrical mirror analyzer (CMA) with an axial electron gun was used to monitor ion-induced electron emission and surface cleanliness. The ion beam was 95° from the CMA axis with the sample normal lying between and coplanar with the two axes at an angle of 60° from the ion beam. Electrons were detected in a 42° annulus about the CMA axis. Typical ion beam currents were 1–20 μA in a 3 mm^2 spot. The targets were polycrystalline Al and Fe mechanically and chemically polished followed by further sputter cleaning with a 100 keV Ar^+ or Kr^+ beam from the accelerator. The Auger spectra shown here were all taken in the differential mode commonly used in Auger measurements and built up over a period of several minutes using a multichannel analyzer to increase signal-to-noise ratio.

2. Ar^+ impact on aluminum

The ion induced spectrum is shown in fig. 1 along with a conventional elctron induced spectrum for comparison; the spectrum is similar to that published earlier by Benazeth and others [4]. Clearly the major feature of the ion induced spectrum is at about the same energy as that in the electron induced spectrum; the feature is certainly due to filling of a 2p shell vacancy which is anticipated on the basis of the pro-

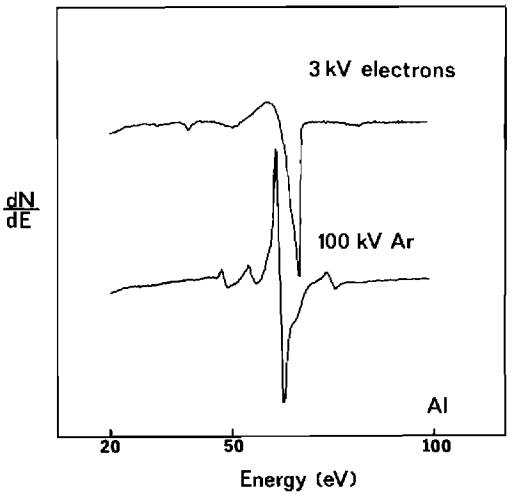

Fig. 1. Auger spectra induced by impact of 3 keV electrons and 100 keV Ar^+ incident on an aluminium target. The spectra are taken in the derivative mode.

motion model. The electron induced line shows a long tail to lower energies which causes the asymmetry in the 67 eV peak; the tail is due to energy loss by electrons emitted below the surface of the target. No such tail is seen on the ion induced spectrum No such tail is seen on the ion induced spectrum. The electron induced spectrum shows a peak at 51 eV, 16 eV below the main peak, representing excitation of bulk plasmons; no such plasmon loss is seen 16 eV below the major peak of the ion induced spectrum. Oxidation of the aluminum surface causes a major change to the electron induced spectrum [3] due to alteration of the valence band structure; the ion induced spectrum remains unchanged on oxidation. Thus the ion induced Auger spectrum shows none of the characteristics expected for emission by an atom in the solid; there is no loss tail, no plasmon loss and no change on oxidation. Vrakking and Kroes [5] have recently argued that the Auger spectrum comes from atom-like structures formed deep in the solid within the disturbed region of the collision cascade. Cross sections for ionization of atoms are of the order 10^{-16} cm^2 or greater so that an electron emerging from deep in the solid will almost certainly cause one or more ionization events with a loss of energy equal to the relevant ionization potential. Thus on oxidizing the surface there should be a large increase of a peak at 13.6 eV below the main Auger structure. While such a peak is indeed present (see fig. 1) it is observed for a clean aluminum surface and shows no change on oxidation. We therefore conclude that the Auger electrons come from aluminum atoms or ions sputtered out of the surface and not from deep in the solid as claimed by Vrakking and Kroes [5].

We propose that the major feature of the ion induced spectrum is due to sputtered neutral Al with a 2p vacancy having a $2p^5 3s^2 3p^2$ configuration. The energy of this state can be estimated as follows. $E(2p^5 3s^2 3p^2) - E(2p^5 3s^2 3p)$ for Al should be approximately equal to the difference between $E(2p^6 3s^2 3p^2)$ and $E(2p^6 3s^2 3p)$ for Si; the latter difference is the ionization potential of Si which from standard tables [6] is 8.149 eV. Taking $E(2p^5 3s^2 3p)$ for Al as 80.5 eV from the calculations of Shirley et al. [7], we arrive at an energy of 72.35 eV for the $2p^5 3s^2 3p^2$ configuration of Al. We can now calculate the energies of five transitions leading to filling of the 2p vacancy and ejection of an outer shell electron.

$$2p^5 3s^2 3p^2 \rightarrow 2p^6 3s^2 : \quad E_{\text{Auger}}\ 66.37\ \text{eV}, \quad (1a)$$

$$\rightarrow 2p^6 3s \quad (^3P^0) : E_{\text{Auger}}\ 61.74\ \text{eV}, \quad (1b)$$

$$\rightarrow 2p^6 3s3p\,(^1P^0) : E_{\text{Auger}}\ 58.95\ \text{eV}, \quad (1c)$$

$$\rightarrow 2p^6 3p^2 \quad (^1D) : E_{\text{Auger}}\ 55.78\ \text{eV}, \quad (1d)$$

$$\rightarrow 2p^6 3p^2 \quad (^3P) : E_{\text{Auger}}\ 54.71\ \text{eV}, \quad (1e)$$

In each case the energy of the final state is readily obtained from standard tables [5]. Transitions (1b) and (1c) explain the principal peak in fig. 1; the cross-over point of the major peak is at about 61 eV. Transitions (1d) and (1e) can explain the secondary peak at 56 eV. Transition la coincides with the shoulder on the main peak at 67 eV. In a similar manner we can identify the small peak at 76 eV as being due to decay of a neutral atom with two 2p vacancies; that is to say a $2p^4 3s^2 3p^3$ configuration. Finally the small peak at 49 eV can be identified as decay of an Al^+ ion with a single 2p vacancy; a $2p^5 3s^2 3p$ configuration. In summary the Auger spectrum induced by Ar^+ on Al has the form expected for target atoms ejected out of the solid and the lines can be completely identified as due to one or two 2p vacancies in Al atoms or Al^+ ions.

3. Ar^+ impact on iron

In fig. 2 we show the Auger spectrum induced by Ar^+ of various energies incident on Fe. Unlike the aluminum case shown in fig. 1 the spectrum is not readily recognizable as being from an Fe target. According to the promotion model [1] vacancies should occur in the 2p shell of the argon projectile; this is the origin of the broad peak at about 216 eV which is simply the $L_{23}M_{23}M_{23}$ transition of Ar. At about 45 eV there is a large peak which coincides exactly with the $M_{23}M_{45}M_{45}$ peak seen in the electron induced Auger spectrum of Fe. According to the promotion model an M_{23} vacancy (i.e. 3p vacancy) in Fe can occur in the direct Ar^+ + Fe primary collision as well as in Fe + Fe collisions occurring in the collision cascade. A second small peak at about 75 eV occurs in both the ion and electron induced spectra of Fe; it is probably the $M_1M_{45}M_{45}$ transition of Fe. There remains a considerable additional structure in the region 90–200 eV that is not readily identified as arising from either Fe or Ar.

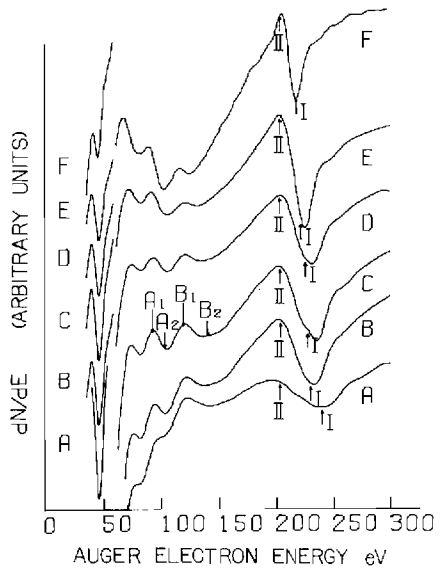

Fig. 2. Auger spectra induced by 20–200 keV Ar^+ incident on an irong target. The spectra are taken in a derivative mode. The peak designated I–II is identified as a Doppler-broadened LMM transition in backscattered argon. Peaks A and B are identified as interatomic transitions involving Ar vacancies filled by electrons from Fe (see text). Curves A to F are for 200, 100, 80, 60, 40 and 20 keV Ar^+ ions respectively.

Let us examine first the Ar $L_{23}M_{23}M_{23}$ peak lying at about 216 eV. We can demonstrate that the changing line width is consistent with a Doppler shift of electron energy due to the source of electrons being backscattered Ar^+ ions. According to Werme et al. [8], the major feature of the $L_{23}M_{23}M_{23}$ transition from an isolated Ar^+ ion is a group of lines lying between 203 and 206 eV. We can predict that if such a group were to be recorded using the derivative mode of our CMA and detector then there would be a conventional single peak with the positive excursion at about 203 eV and the negative excursion at 206 eV. We perform the calculation for the case of ions scattered through 43° from their original direction and emitting their Auger electron in the direction of their motion. This seemingly arbitrary choice represents scattering and electron emission in the plane of the incident ion beam, target surface normal and CMA axis, with the direction of motion directly towards one side of the CMA annular entrance aperture. This choice will serve for an illustration of qualitative behaviour. The scattered Ar^+ ion energy is calculated from conservation of energy and momentum; the Doppler effect is computed from the formula given by Dahl et al. [9]. This Doppler shift is then added to the negative excursion of the expected peak from an isolated Ar ion and gives the points labeled I in fig. 2. For the geometry of the present experiment there will be very few particles scattered out of the surface and away from the detector giving a shift to lower electron energies. Thus the positive excursion of the Ar $L_{23}M_{23}M_{23}$ peak should remain essentially unchanged with projectile energy; the expected position of the positive excursion is indicated by the symbol II in fig. 2. The positions of points I and II evaluated in this manner do in fact agree quite well with the observed positions of the positive and negative excursions, confirming that the changes in peak shape and position are consistent with the Doppler effect. It is also clear that in the limit as projectile energy tends to zero the argon line extrapolates to the position expected for a free Ar^+ ion. We offer no definite explanation of the weak double peak seen on the argon line for 60 and 80 keV impact. We do note, however, that the backscattered energy spectrum of Ar^+ ions from polycrystalline materials is a broad continuum with superimposed a sharp peak due to surface scattering [10]; such an energy distribution

would produce a double peak structure on the negative excursion.

In the region 90–200 eV there are other peaks which cannot be identified as due to Fe or to Ar. The peaks are not seen in an electron induced Auger spectrum of the target and are not seen when a different heavy projectile is used (e.g. Kr^+). We will argue that these features are interatomic Auger transitions involving a core hole in the projectile being filled by electrons for a neighboring Fe atom. The transitions are of the type $L_{Ar}M_{Fe}M_{Fe}$ or $L_{Ar}M_{Fe}M_{Ar}$ where L_{Ar}, L_{Fe}, etc., are energy levels of Ar and Fe atoms. Transitions of this type have been seen in a number of systems [11]. The interatomic transition rate depends on the spatial overlap of the initial hole state (L_{Ar}) and the annihilating electron state (M_{Ar} or M_{Fe}) as well as the initial state of the ejected electron and its continuum wave function. There appear to be two lines designated A and B in fig. 2; line A extends from the positive excursion A_1 to the negative excursion at A_2 and similarly the line B extends from B_1 to B_2. Clearly the width of line A (measured as the energy $E_{A_2} - E_{A_1}$) is small and decreases slightly from 13 to 6 eV as the projectile energy increases from 20 to 200 keV. By contrast the width of line B ($E_{B_2} - E_{B_1}$) increases with increasing projectile energy with the negative excursion moving to higher energy and the positive excursion remaining unchanged; this behaviour is exactly similar to that of the argon Auger line therefore representing a Doppler effect and indicating that the source of the electrons is a moving projectile. We ascribe peak A to an Ar (L_{23}) Fe (M_1, M_{23}) transition whose energy can be estimated (from the binding energies of Shirley et al.) [7], to be 95.5 eV. The small decrease in peak width with increasing projectile energy is consistent with the "Berry effect" whereby the emitted electron is affected by the Coulomb fields of both the source ion (Fe) and the Ar projectile [13]. There is no Doppler effect because the source of the monitored electron is an Fe atom in the matrix. We ascribe peak B to a transition of the type Ar (L_{23}) Fe (M_1) Ar (M_{23}) whose energy from a stationary system should be [7] about 138 eV. The broadening with projectile energy occurs because the source of the detected electron is an argon projectile which is in motion. There are in fact at least eight interatomic transitions which occur in the region 90–200 eV and we do not claim positive identification of these two major peaks. We do, however, conclude that the structures *A* and *B* are interatomic transitions with the ejected electron coming from an Fe atom for peak A and from the Ar atom for peak B.

4. Conclusion

The ion induced Auger spectra of metals occur due to electron promotion mechanisms and exhibit different lines from those seen in electron induced spectra. For Ar^+ on Al the vacancies occur in the L_{23} shell of Al and the spectrum is identified as being due to sputtered Al and Al^+. For Ar^+ on Fe the promotion model predicts vacancy formation in the 2p level of Ar. We observe a Doppler-broadened LMM line of Ar from backscattered atoms and also certain interatomic transitions involving decays in the Ar Fe quasi-molecular system.

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Auger spectra induced by 100-keV Ar^+ impact on Be, Al, and Si

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The Auger electron spectrum induced by the impact of 100-keV Ar^+ on metallic aluminum is shown to be consistent with the source of Auger electrons being ejected target particles. The principal spectral line has been identified as being due to ejected Al atoms with a single $2p$ vacancy. Subsidiary peaks are due to ejected atoms and Al^+ ions with one or two $2p$ vacancies. The ion-induced Auger spectrum of silicon is similar. By contrast the spectrum induced by Ar^+ impact on Be exhibits a rather broad peak characteristic of a K-shell vacancy and is similar to that induced by the impact of electrons. By considering the lifetime of the Be K-shell vacancy we conclude that the Auger decay occurs while the Be atoms are either in the solid or interacting with the surface.

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I. INTRODUCTION

The impact of heavy ions on surfaces gives rise to intense emission of Auger electrons. Early descriptions of the Auger spectra were given by Louchet *et al.*[1] and by Grant *et al.*,[2] concentrating on spectra induced by Ar^+ impact on light target materials such as Be, Mg, Al, and Si. The ion-induced spectra are normally rather different from the corresponding electron-induced spectra; line shapes are changed, the main peak for the ion-induced spectrum is generally lower than that for electron impact, and the subsidiary structure is different in the two cases. The present work studies further the spectra induced by Ar^+ impact on Be, Al, and Si with the conclusion that for Al and Si the Auger electrons are predominantly due to sputtered Al and Si atoms with $2p$ vacancies.

Louchet *et al.*[1] realized at the outset that the mechanism by which incident ions induce vacancies is quite different from that by which electrons create vacancies. Electron-induced spectra occur by a Coulomb excitation of a core electron followed by an Auger decay while the atom remains in the target matrix. For heavy ion impact at the energy of the early experiments (generally 3–60-keV Ar^+) the cross sections for Coulomb excitation are too small to explain the observed ion-induced spectrum. Rather, one must invoke an electron promotion mechanism where impact of projectile A on target B leads to temporary formation of the molecule AB; the energy levels of the electrons are perturbed as the nuclei approach each other causing some levels to become degenerate and thereby permit an electron to transfer to a vacant level. As the atoms separate the energy levels return to those appropriate to the isolated atoms A and B but now with a vacancy in an inner shell. It is this vacancy which is filled by a subsequent Auger transition leading to emission of an Auger electron. The reader is referred to the comprehensive treatise by Barat and Lichten[3] for a discussion of how the correlation diagrams for the quasi-molecule AB may be constructed and interpreted to predict where vacancies will occur.

The present work studies Auger spectra induced by 20–200-keV Ar^+ impact on Be, Al, and Si. The promotion mechanism predicts[3] that vacancies will occur in the $2p$ shell of Al and Si; for Be the vacancies will be in the $1s$ shell. According to the promotion model, Ar^+ impact on targets of nuclear charge greater than that of the projectile should result in vacancy creation in the inner shells of the projectile not of the target; a study of such cases is to be presented in a subsequent paper.[4]

II. EXPERIMENTAL ARRANGEMENT

The layout of the experiment is shown in Fig. 1. A UHV chamber capable of base pressures below 10^{-10} Torr was linked via a differentially pumped beam line to a 20–200-keV ion implanter. Target samples were placed on a standard manipulator and positioned at the center of the chamber. A

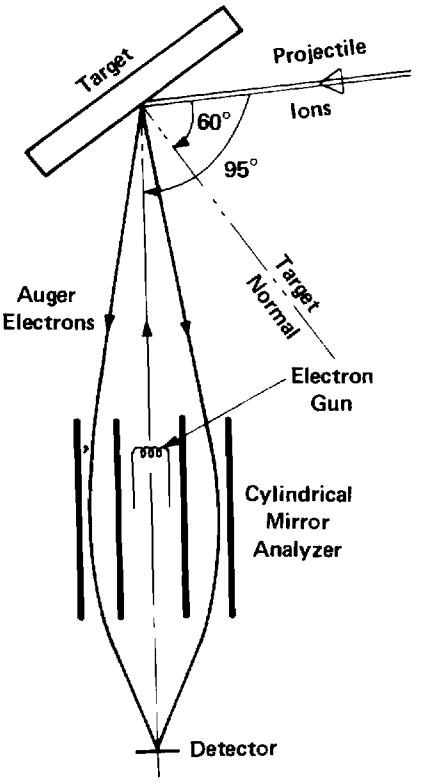

FIG. 1. Schematic diagram of the experimental arrangement (not to scale).

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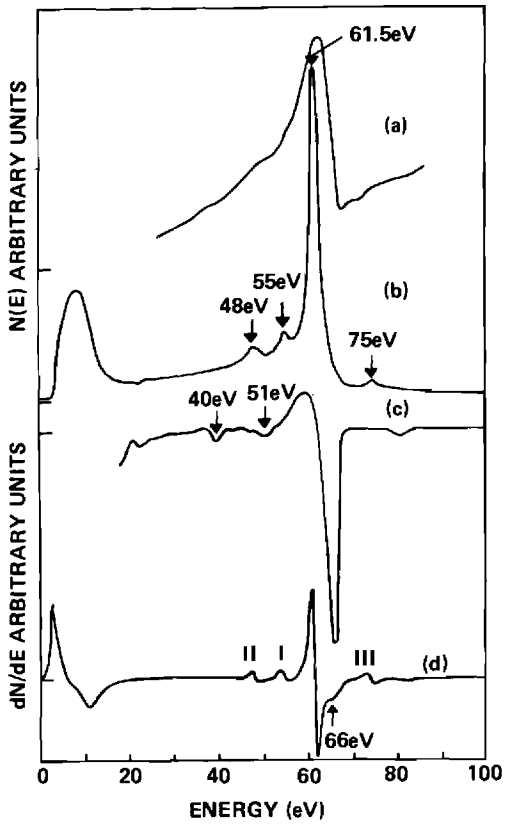

FIG. 2. Auger spectra induced by 3-keV electrons and 100-keV Ar^+ ions on aluminum. Spectra (a) and (b) are for electrons and ions, respectively, with the spectra taken in the integral mode. Spectra (c) and (d) are again for electron and ion impact, respectively, but taken in the derivative mode.

standard commercial cylindrical mirror analyzer (CMA) with an axial electron gun was placed so that it could be used both to record the electron-induced Auger spectrum of the target (utilizing the integral electron gun) as well as the ion-induced Auger spectrum (utilizing an ion beam from the accelerator). The ion beam was 95° from the CMA axis with the sample normal lying between, and coplanar with the two at an angle of 60° from the ion beam. The CMA detected electrons emitted into a 42° annulus about its axis. Ion beam currents were between 1 and 20 μA with a beam diameter of about 3 mm. The electron beam was 10 μA with a diameter of 0.1 mm. For the work described here the ion beam energy was generally 100 keV and the electron beam energy was 3 keV. Pressure in the target region varied from 7×10^{-10} to 6×10^{-9} Torr with the beam on; most of the residual gas was of the projectile species (Ar).

Samples of Be, Al, and Si were mechanically and chemically polished polycrystals cleaned *in situ* by 100-keV Ar^+ from the accelerator. After cleaning, the surfaces carried no more than 2% monolayer of C and 20% O contamination as determined by AES.[5] Further cleaning was found to have no significant effect on the results. Auger spectra were normally taken in the derivative mode commonly used in Auger measurements and built up over a period of several minutes using a multichannel analyzer to increase the signal/noise ratio. For a few target species we recorded also the integral Auger spectra, again using a multichannel analyzer to improve the signal/noise ratio. The inherent resolution limit of the CMA was about 0.3%, but resolution was limited in the differential mode by the 5-V rms modulation used.

III. THE OBSERVED AUGER SPECTRA

In Fig. 2 the spectra induced by Ar^+ and electron impact on aluminum are shown in both integral and derivative modes of recording. In Fig. 3 we display the integral spectra observed when the aluminum target is oxidized. The primary feature in the derivative spectra is an intense line at either 61.5 eV (for Ar^+ impact) or 67 eV (for e impact). The binding energy for the $L_{2,3}$ shell[6] is about 80.5 eV so that this major peak is undoubtedly due to a $2p$ vacancy. Additional subsidiary structure is seen at lower and higher energies most clearly in the derivative spectra. According to Guennou *et al.*,[7] the major peak in the electron-induced derivative spectrum (at 67 eV) is an L_{23} VV Auger transition (where V indicates valence electron) and the 51-eV subsidiary peak is due to L_{23} VV electrons that have excited a bulk plasmon; the 40-eV peak is identified as L_1L_{23} V transition.

It is instructive to examine the differences in detail between the ion- and electron-induced spectra of aluminum. The electron spectrum [Fig. 2(a)] shows a distinct tail towards lower energies which is related to energy loss by L_{23} VV electrons as they traverse the distance from their point of excitation to their escape from the surface; electrons excited below the surface emerge at lower energies than those excited at the surface. No such "loss tail" is seen on the ion-induced spectrum [Fig. 2(b)]. Raising the ambient pressure in the target chamber to 10^{-5} Torr with oxygen we observe significant changes to the electron-induced spectrum [see Fig. 3(a) in comparison with Fig. 2(a)]. This is caused by formation of a surface oxide and is related to changes in valence band structure. A similar test for the ion-induced spectrum showed no significant change in the Auger spectrum when compared with the spectrum taken in the absence of oxygen [see Fig. 3(b) compared with Fig. 2(b)]. We did check that simultaneous electron and ion bombardment in the presence of oxygen showed a spectrum composed of the superposition of Figs. 3(a) and 3(b). This confirms that the Ar^+ beam is not simply sputtering the oxygen from the surface to leave clean aluminum. Thus we conclude that the ion-induced spectrum from an oxide covered surface of aluminum is identical with that for clean aluminum and that the

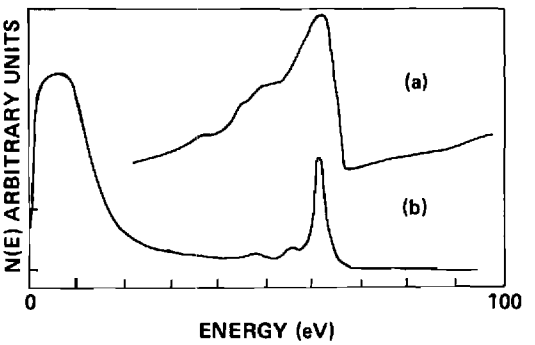

FIG. 3. Integral Auger spectra induced by impact of 3-keV electrons [spectrum (a)] and 100-keV Ar^+ ions [spectrum (b)] incident on oxidized aluminum.

ion-induced Auger spectrum does not involve the valence band of the solid. The 40-eV peak in the electron-induced spectrum [Fig. 2(c)] is not observed in the ion-induced spectrum. This peak is due to[7] a L_1 (i.e., $2s$) shell vacancy that will not be created by the promotion mechanism in an $Ar^+ + Al$ collision; thus its absence is expected. The 51-eV peak in the electron-induced spectrum is related to plasmon excitation[7] involving a 15–16-eV energy loss. In the ion-induced spectrum there is a peak 13.5 eV below the main feature but this is not at the correct energy for either a bulk or a surface plasmon in aluminum. Thus the ion-induced spectrum exhibits none of the characteristics expected when the Auger emission takes place while the excited atom is in the solid; there is no loss tail, no change when the surface is oxidized, and no peaks associated with excitation of plasmons. We would conclude that the Auger decay takes place when the excited atom is outside the surface. Consequently the electrons originate from atoms or ions ejected from the solid.

Previous work on the Auger spectrum induced by Ar^+ impact on Al has been performed by the group at Toulouse.[1,8–11] Their experimental arrangement differs significantly from the present system only in that it selects electrons ejected at 33° from the incident beam direction[8] rather than into the 42° annulus centered at 95° from the beam direction which was used in the present work. The observed spectra are generally the same as those shown in Figs. 2(b) and 2(d) except that the subsidiary lines at 48 and 55 eV are superimposed on a continuous background that amounts to about 30% of the 61.5-eV peak height; no such background is seen in the present work. The Toulouse group see a shoulder on the high-energy side of the 61.5-eV peak which they ascribe to an L_{23} VV transition involving the valence band electrons; that would require Auger transitions from atoms in the solid. No such shoulder is observed in the present integral spectra although an inflection is seen on the derivative spectrum [Fig. 2(d)] at 66 eV which almost corresponds to the position of the major downward peak in the electron-induced Auger spectrum [Fig. 2(c)].

Figure 4 shows the ion-induced spectra of silicon. The

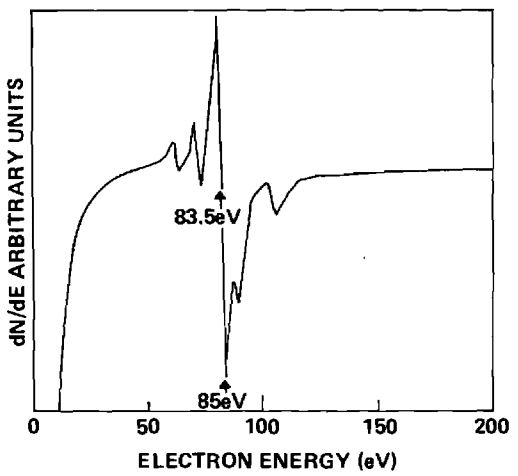

FIG. 4. Differential Auger spectrum induced by 100-keV Ar^+ impact on silicon.

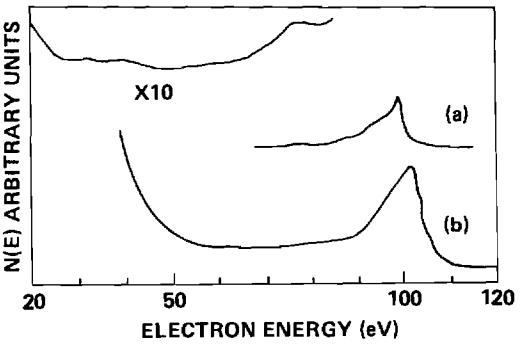

FIG. 5. Auger spectra induced by (a) 3-keV electrons and (b) 100-keV Ar^+ ions on beryllium. The spectra are taken in the integral mode.

general features are similar to those found for aluminum. The ion-induced spectrum shows a number of sharp lines whose form is consistent with the electron emission occurring from atoms or ions that have been ejected from the solid. Figure 5 shows electron- and ion-induced spectra for a beryllium target. Here the emission results from K-shell vacancies in Be and there appears to be a broad line.

IV. DISCUSSION

We shall concentrate first on the aluminum case. The vacancies are formed in the $L_{2,3}$ shell and the general form of the spectrum is consistent with the source of electrons being from atoms or ions ejected out of the surface. The $L_{2,3}$ vacancies can be created by electron promotion in $Ar^+ + Al$ collisions; vacancies will not be formed in the L_1 shell.[3] Al atoms recoiling in the collision cascade within the solid will collide with other Al atoms and if the collision energy is sufficiently high, this may also result in $L_{2,3}$ shell vacancy production through symmetric Al + Al collisions. Thus the vacancies can occur both by the collision of the projectile on the target and also by collisions of recoiling target atoms. The same spectrum is seen[12] for Ne^+ impact on Al where promotion of L_{23} electrons in the primary $Ne^+ + Al$ impact is not possible[3]; this suggests that at least part of the observed Auger spectrum is induced by collisions of recoiling target atoms. The promotion mechanism occurs only during a rather close approach of the participating nuclei which in turn means that the collisions are violent with considerable energy transfer to the target nuclei. Vrakking and Kroes[12] have studied the threshold energy for excitation of the Auger lines and concluded that at least 300 eV energy is required in the center of mass frame for $L_{2,3}$ shell promotions in both the Ar + Al and Al + Al collisions. Thus the vacancies are created in atoms moving in the laboratory frame with at least 600 eV of energy or a minimum speed v of 6.5×10^6 cm/sec; taking the lifetime of the $L_{2,3}$ vacancy τ as 1.33×10^{-13} sec,[13] the decay length of the $L_{2,3}$ vacancy is at least 86 Å (the product $v\tau$). By contrast the escape depth of an aluminum Auger electron is about 4.2 Å.[14] Thus atoms recoiling into the solid will in general emit their Auger electron at a depth from which it cannot escape. It follows that only when the excited Al atom recoils out of the target (i.e., is sputtered) will the Auger electron be detected. This conclusion is consistent with our analysis of the spectrum which also leads to

the conclusion that the Auger electrons come from particles that have been ejected from the solid.

We must now attempt to identify the states of excitation in the ejected particles. Reference to previous studies of gas-phase bi-particle collisions[15] show a complex Auger spectrum having eight or more lines that in no way resembles the spectra shown in Fig. 2; these gas-phase spectra are identified as being from ionized states of aluminum. We have therefore examined the possibility that the major feature of the ion-induced Auger spectrum of metallic Al is from sputtered Al atoms with a $2p$ shell vacancy. In the absence of a published value of the energy of the $2p^5\ 3s^2\ 3p^2$ configuration we have estimated a value as follows. The difference between $E(2p^5\ 3s^2\ 3p^2)$ and $E(2p^5\ 3s^2\ 3p)$ for Al should be approximately equal to the difference between $E(2p^6\ 3s^2\ 3p^2$ and $E(2p^6\ 3s^2\ 3p)$ of Si; this latter difference is simply the energy for removing one electron from Si and is given to be 8.15 eV in standard references.[16] Taking the energy of the $2p^5\ 3s^2\ 3p$ configuration to be 80.5 eV from the calculations of Shirley *et al.*,[6] we arrive at an energy of 72.35 eV for the $2p^5\ 3s^2\ 3p^2$ configuration of Al. We now calculate the energies for the following five transitions leading to filling of the $2p$ vacancy and ejection of an outer shell electron:

$$
\begin{aligned}
2p^5\ 3s^2\ 3p^2 &\rightarrow 2p^6\ 3s^2 \quad E_{\text{Auger}} && 66.37\text{ eV} && \text{(1a)}\\
&\rightarrow 2p^6\ 3s\ 3p(^3P^0) \quad E_{\text{Auger}} && 61.74\text{ eV} && \text{(1b)}\\
&\rightarrow 2p^6\ 3s\ 3p(^1P^0) \quad E_{\text{Auger}} && 58.95\text{ eV} && \text{(1c)}\\
&\rightarrow 2p^6\ 3p^2(^1D) \quad E_{\text{Auger}} && 55.78\text{ eV} && \text{(1d)}\\
&\rightarrow 2p^6\ 3p^2(^3P) \quad E_{\text{Auger}} && 54.71\text{ eV.} && \text{(1e)}
\end{aligned}
$$

In each case the energy of the final state is readily obtained from standard tables.[16] We observe that transitions (1b) and (1c) can explain the principal peak in Fig. 2(b) (at 61.5 eV), transitions (1d) and (1e) can explain the first subsidiary peak [designated I in Fig. 2(b)] and lying at 55 eV; furthermore, transition (1a) agrees exactly with the shoulder to the main peak which is most clearly exhibited at 66 eV in the derivative spectrum [Fig. 2(d)]. It has previously been argued that this latter shoulder is in fact due to Auger electrons from the valence band of the solid[2]; the above argument provides an alternative explanation consistent with our picture of deexcitation outside the solid.

We have also examined the possibility that Al^+ with a $2p$ vacancy contributes to the spectrum through the two transitions

$$
\begin{aligned}
2p^5\ 3s^2\ 3p &\rightarrow 2p^6\ 3s \quad E_{\text{Auger}} && 55.7\text{ eV} && \text{(2a)}\\
&\rightarrow 2p^6\ 3p \quad E_{\text{Auger}} && 49.0\text{ eV.} && \text{(2b)}
\end{aligned}
$$

The energy of the parent state is taken from the theoretical binding energies of Shirley *et al.*[6] and the energies of the daughter states from Moore.[16] Transition (2b) can explain peak II in Fig. 2(b) and transition (2a) may contribute to peak I. Finally the high-energy structure [designated III in Fig. 2(d)] exhibited at 75 eV has been identified by Viel *et al.*[9] as being due to decay of ejected particles with two inner shell $2p$ vacancies.

While we have not discussed all possible configuration of ejected atoms and ions it is clear that the observed spectrum can be properly ascribed to ejected target particles. The observed spectrum can be completely explained as being due to ejected Al atoms and Al^+ ions with one or two $2p$ vacancies. The breadth of the lines (approximately 2.3 eV FWHM) is perhaps a Doppler broadening due to the energy of the emerging particles. A recoil energy of 300 eV would produce a broadening of the order 2.5 eV.[15,17]

The Auger spectrum of Si exhibits the same general form as that of Al. We can again predict Auger electron energies for decay of neutral Si with a $2p$ vacancy and Si^+ with a $2p$ vacancy. The excited Si state has a configuration $2p^5\ 3s^2\ 3p^3$. Its energy can be estimated as 98.3 eV using the relationship that $E(2p^5\ 3s^2\ 3p^3) - E(2p^5\ 3s^2\ 3p^2)$ for Si is approximately the same as $E(2p^6\ 3s\ 3p^3) - E(2p^6\ 3s^2\ 3p^2)$ for P; the energies of the levels can be taken from Shirley *et al.*[6] and from Moore.[16] The energy of the $E(2p^5\ 3s^2\ 3p^2)$ state of Si^+ is 106.5 eV from Shirley *et al.*[6] Again using Moore[16] to estimate energies of the final states we arrive at the transitions

$$
\begin{aligned}
2p^5\ 3s^2\ 3p^3 &\rightarrow 2p^6\ 3s^2\ 3p\ (^2P^0) \quad E_{\text{Auger}} && 90.15\text{ eV} && \text{(3a)}\\
&\rightarrow 2p^6\ 3s\ 3p^2\ (^4P) \quad E_{\text{Auger}} && 84.70\text{ eV} && \text{(3b)}\\
&\rightarrow 2p^6\ 3s\ 3p^2\ (^2D) \quad E_{\text{Auger}} && 83.30\text{ eV} && \text{(3c)}\\
&\rightarrow 2p^6\ 3s\ 3p^2\ (^2S) \quad E_{\text{Auger}} && 80.65\text{ eV} && \text{(3d)}\\
&\rightarrow 2p^6\ 3s\ 3p^2\ (^2P) \quad E_{\text{Auger}} && 79.71\text{ eV} && \text{(3e)}\\
&\rightarrow 2p^6\ 3p^3\ (^4S^0) \quad E_{\text{Auger}} && 74.75\text{ eV} && \text{(3f)}\\
2p^5\ 3s^2\ 3p^2 &\rightarrow 2p^6\ 3s^2\ (^1S) \quad E_{\text{Auger}} && 82.01\text{ eV} && \text{(4a)}\\
&\rightarrow 2p^6\ 3s\ 3p\ (^3P^0) \quad E_{\text{Auger}} && 75.47\text{ eV} && \text{(4b)}\\
&\rightarrow 2p^6\ 3s\ 3p\ (^1P^0) \quad E_{\text{Auger}} && 71.74\text{ eV} && \text{(4c)}\\
&\rightarrow 2p^6\ 3p^2\ (^1D) \quad E_{\text{Auger}} && 66.90\text{ eV} && \text{(4d)}\\
&\rightarrow 2p^6\ 3p^2\ (^3P) \quad E_{\text{Auger}} && 65.94\text{ eV} && \text{(4e)}\\
&\rightarrow 2p^6\ 3p^2\ (^1S) \quad E_{\text{Auger}} && 63.00\text{ eV} && \text{(4f)}
\end{aligned}
$$

There are obviously far more lines here than there are peaks in Fig. 4 but many lines are sufficiently close that they would be unresolved due to broadening by the Doppler effect. We note particularly that transition (3b)–(3e) fall in the region of the main peak and that transition (3a) falls exactly at the first subsidiary peak to the high-energy side of the main peak (at 90 eV). Transitions (4b)–(4f) lie in the region of the subsidiary peaks I and II. The high-energy peak III can be identified as decay of Si atoms with two $2p$ vacancies. Consequently the spectrum from silicon can be completely explained as being due to ejected Si and Si^+ with one and two $2p$ vacancies; this is the same explanation as we invoke for aluminum.

The Be spectrum (Fig. 5) must of course be related to the formation of K-shell vacancies. The discussion of correlation diagrams by Barat and Lichten[3] shows how the K-shell vacancy can occur by a $3d\ \sigma$ promotion. This beyllium spectrum differs notably from that of aluminum in the breadth of the main Auger line; it is approximately 10 eV wide (FWHM) compared with the 2.3-eV width of the major peak from Al. If we arbitrarily assume that the recoil energy of beryllium atoms with the K-shell vacancy is 300 eV and that the lifetime of the K-shell vacancy is about 10^{-14} sec (the value calculated by McGuire[18] for boron) then the distance moved during the lifetime of the K-shell vacancy is only some 8 Å. It follows then that if the Be atom recoils out of the target then the majority of decays will occur while the ejected atom is still interacting with the surface. Thus the Auger line shape will reflect distortion of the energy levels by the

surface leading to a line broadening towards lower Auger energies as discussed by Dorozhkin *et al.*[19] Furthermore, the escape depth for 101-eV electrons from Be is about 3.76 Å[14] and therefore is quite comparable with the decay length for K-shell vacancies of 300-eV Be. It follows then that Be atoms or ions recoiling into the target from surface collisions will emit their Auger electrons while close enough to the surface that such electrons can escape and be detected. Consequently a large proportion of the Auger electrons may be emerging from atoms in the matrix or atoms interacting with the surface; this would lead to an Auger line shape similar to that excited in the solid by impact of electrons. Detailed identification of the emitting states is not possible because of the extreme width of the observed line. We note however, that the peak intensity occurs at 101 eV which coincides exactly with decay of a $1s\ 2s^2\ 2p$ neutral atom state as observed in gas-phase collisions.[20] Moreover, we do not observe a line at 96 eV which is expected from Be^+ ions with a single K-shell vacancy.[20] Thus the observed spectrum is consistent with the source of electrons being Be atoms with single K-shell vacancies.

Recently Vrakking and Kroes,[12] following earlier suggestions by Hennequin and Viaris de Lesegno,[21] have argued that the main line of the ion-induced Auger spectrum comes from free recoiling target atoms deep within the solid in the highly disturbed region of the collision cascade. The free electron density is said to be reduced by a factor of 3 from the value for an unperturbed solid causing a decrease in plasmon energy. We believe that this model by Vrakking and Kroes is not consistent with the observed spectra. If excitation of plasmons is invoked to explain the small peaks on the ion-induced spectra then one would expect that changes to free electron density by oxidation or by alloying with other metals should inevitably cause shifts and shape changes to the peaks. We observe no significant change to the aluminum spectrum when the surface is oxidized and Viel *et al.*[22] observe no change to the aluminum lines when they are excited in an aluminum-magnesium alloy; this implies that the subsidiary peaks are not related to electron density and are therefore not plasmon losses. The model of Vrakking and Kroes[12] would seem to explain only peak I as a plasmon loss. Peak II is also referred to as a loss peak but its origin is not explained. The Vrakking and Kroes model requires that the electrons emerge from depths of 30 Å or more (for 5-kV Ar^+ impact), more than five times the normally accepted escape depth for the aluminum Auger electrons. It is well known[23] that the cross section for electron ionization of atoms is always of the order 10^{-16} cm^2 or higher. Thus any electrons emerging from deep in the solid will have almost unit probability of ionizing an atom in this disturbed region of the collision cascade and therefore will emerge with an energy loss equal to the relevant ionization potential of the target atom. For Al we should expect a peak at 5.98 beV below the main peak; our observed peak I [Fig. 2(b)] lies 6.5 eV lower. Furthermore when the surface is oxidized there should be an additional peak related to ionization of oxygen at an energy loss of 13.61 eV; while peak II [Fig. 3(b)] lies 13.0 to 13.5 eV below the main feature it is present even when the surface is not oxidized and does not change its relative height on oxidation. Study of the spectra for silicon and beryllium targets leads to the same conclusion that there are no structures representing energy loss by ionization, which should be an inevitable consequence of the model by Vrakking and Kroes.[12] All observed structures for the aluminum and silicon targets can be completely explained as coming from free ejected atoms and ions that have one or two inner shell vacancies.

Recently Wittmaack[24] has studied the Auger spectrum of Si induced by 2–30-keV noble gas ion bombardment. The conclusions are generally the same as those of the present work in that the major features are identified as being due to sputtered target atoms with single L-shell vacancies, and the subsidiary features are not loss peaks (as suggested by Vrakking and Kroes) but are the result of the same type of excitation process as the principal line. Wittmaack attempts to identify the lines using transition energies calculated[25] for solid Si. We regard this as an incorrect approach since the origin of the lines is said to be free atoms sputtered from the target. The calculated line positions presented in the present paper are based on energies for free atoms and are therefore consistent with the supposed origin of the line. The spectra published by Wittmaack are taken with a 1-V peak-to-peak modulation and show a certain fine structure which is not observed in the present work where the modulation was 5 V peak to peak.

V. CONCLUSION

The Auger spectra induced by ion impact on Be, Al, and Si exhibit a line spectrum characteristic of the target species. For the case of Be the spectrum is due to K-shell vacancies and closely resembles that observed due to electron impact on solids. Consideration of the K-shell lifetime and possible recoil speeds leads us to conclude that the Auger electron is emitted while the parent atom is either in the solid or at least still interacting with the surface of the solid. Hence it is not surprising that the observed spectrum resembles that induced by electron impact where the emitting species is certainly in the solid matrix. By contrast, the ion-induced spectra of Al and Si do not show the features expected if the parent atom interacts with the solid matrix during emission. We conclude that the Auger electrons arise from atoms that have been sputtered from the surface and undergo their decay as free atoms remote from the surface. The spectrum from Al can be completely explained by reference to published energy level information. The major peak is due to decay of ejected Al atoms with a single $2p$ vacancy. Subsidiary structure is due to Al atoms with two $2p$ vacancies and to Al^+ ions with a single $2p$ vacancy. The spectrum from Si is similar. We find no evidence to support the contention of Vrakking and Kroes[12] that the Auger lines from Al arise from recoiling Al atoms within the collision cascade of the solid.

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Identification of Auger spectra induced by Ar^+ and Kr^+ ion impact on transition metals

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The production of Auger electrons from Cr, Mn, Fe, and Co by 20–200-keV Ar^+, 100-keV Kr^+, and 3-keV electrons has been studied. The metal $M_{23}M_{45}M_{45}$ and the Argon LMM peaks are clearly identifiable, the latter broadened consistent with electron emission from backscattered Argon ions. Various other features are produced which cannot be due to target or projectile Auger emission. These are believed to result from interatomic transitions between the ions of the beam and those of the target.

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I. INTRODUCTION

Although Auger electron emission from gaseous targets under ion bombardment has been studied for many years,[1] relatively little data exist for ion bombarded solids. Because electron emission is particularly strong from some light elements, most of the work to date has concentrated on Be, Mg, Al and Si Refs. 2–12, although Li and Na, (Ref. 5) K, Ca, Sc, and V (Ref. 13), Ge (Ref. 14), Ag (Ref. 5), Ti (Refs. 8, 12, and 13), Cr (Refs. 8, 13), Fe (Ref. 8), and Cu (Refs. 5, 8, 14), the alloys Al-15% Mg and Fe_3Al (Ref. 10) and the compound GaP (Ref. 12) have also been examined. The bombarding species has usually been Ar^+ in the energy range from a few keV to several hundred keV, although some workers have used He^+ (Ref. 6), Ne^+, and Xe^+ (Ref. 9), Kr^+ (Refs. 8 and 9), and protons.[15] The energy spectra of the emitted electrons usually comprise a low-energy secon-

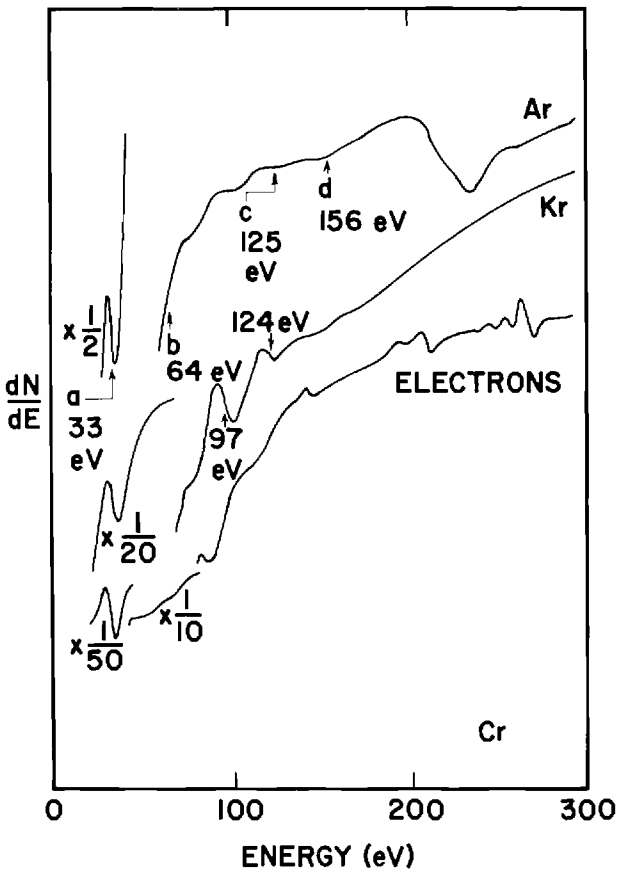

FIG. 1. Auger spectra induced by impact of 3-keV electrons and 100-keV Ar^+ and Kr^+ on a chromium target. The various indicated features are identified in the text.

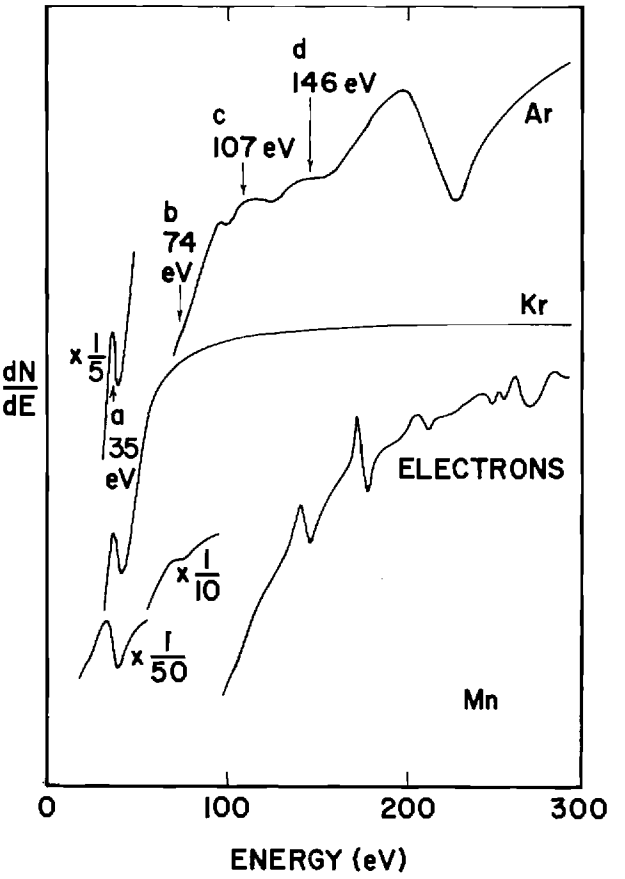

FIG. 2. Auger spectra induced by impact of 3-keV electrons and 100-keV Ar^+ and Kr^+ ions on a manganese target. The various indicated features are identified in the text.

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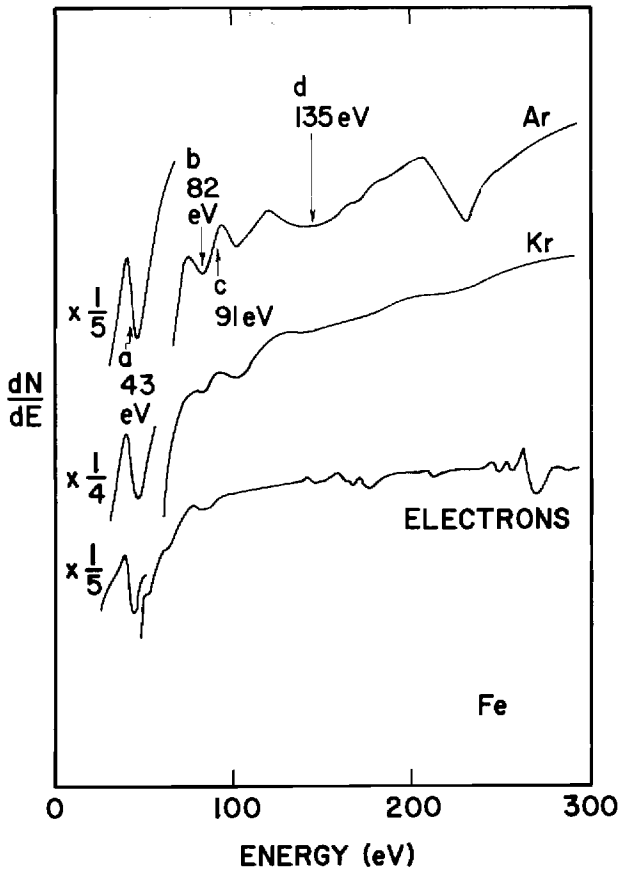

FIG. 3. Auger spectra induced by impact of 3-keV electrons and 100-keV Ar^+ and Kr^+ ions on an iron target. The various indicated features are identified in the text.

dary electron peak, on which some workers have found a great deal of structure,[16–18] with higher-energy Auger peaks from the target and the bombarding species up to about 300 eV.

The mechanism for formation of the inner-shell hole required to create an Auger electron is understood in terms of the electron promotion model of Barat and Lichten.[19] In this model, the electron energy levels of the two ions are perturbed as they approach each other, allowing levels on different ions to become degenerate. This permits electron promotion from a filled inner shell on one atom to an unfilled shell on either atom, creating an inner-shell hole which can subsequently decay by an Auger process.

The ion-induced Auger spectrum is not identical to that observed with electron bombardment,[7,11] the metal peaks tending to be sharper, more symmetric and largely independent of surface contamination.[20] We have proposed that in the case of Be, Al, and Si targets bombarded by Ar^+ the Auger electrons are primarily from sputtered neutral atoms.[21]

In the work reported here we have examined in some detail the ion-induced Auger spectrum of transition metals (Cr, Mn, Fe, and Co) in order to understand the mechanisms giving rise to the Auger emission.

II. EXPERIMENTAL METHODS

Our experimental arrangement consisted of an UHV chamber capable of base pressures below 10^{-10} Torr linked via a differentially pumped beam line to a 20–200-keV ion-implantation accelerator. A standard commercial cylindrical-mirror electron energy analyzer (CMA) with an axial electron gun was used to monitor ion-induced electron emission and surface cleanliness.

The ion-beam axis was 95° from the CMA axis with the sample normal lying between, and coplanar with, the two axes at an angle of 60° or 65° from the ion beam. Thus electrons were detected in an annulus 53°–137° from the ion beam. Ion-beam currents were between 1 and 20 μA, while the pressure varied from 7×10^{-10} to 6×10^{-9} Torr with the beam on. Ion-beam energies of 20–200 keV were used for all the data reported here. Comparison electron-induced Auger spectra were taken with a 3-keV 10-μA beam. Modulation of the CMA was 5 V peak to peak. Polycrystalline samples of Cr, Mn, Fe, and Co were mechanically and chemically polished and cleaned *in situ* by 100 keV Ar^+ or Kr^+ bombardment to remove most of the carbon and oxygen contamination. Specta were taken in the differential mode commonly used in Auger measurements and built up over a period of several minutes using a multichannel ana-

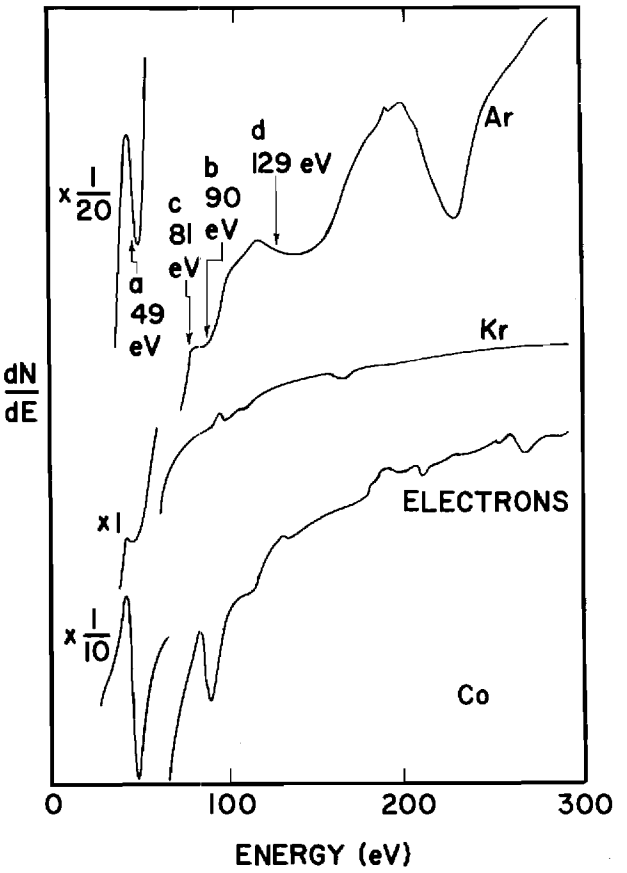

FIG. 4. Auger spectra induced by impact of 3-keV electrons and 100-keV Ar^+ and Kr^+ ions on a cobalt target. The various indicated features are identified in the text.

TABLE I. Relative intensities under 100-keV Ar $^+$ bombardment.

	Metal $M_{23}M_{45}M_{45}$ peak	Ar LMM peak
Cr	1	1
Mn	1.2	0.9
Fe	0.6	0.2
Co	0.2	0.02
	L_{23} MM peak	
Si	7.3	0

lyzer to increase the signal/noise ratio. The surface chemical composition was routinely monitored by Auger spectroscopy. After cleaning the surfaces contained no more than 0.02 monolayers of carbon and 0.2 monolayers of oxygen. The targets were periodically heated to 150 °C, but no attempt was made to anneal ion-induced defects.

III. RESULTS

The Auger spectra of Cr, Mn, Fe, and Co are shown in Figs. 1–4 for 100-keV Ar $^+$ and Kr $^+$ bombardment; for each case we show for comparison a spectrum induced by 3-keV electron impact. The spectra are as directly measured by the CMA and therefore the energies are referenced to vacuum. Certain features are readily identifiable. The lowest-energy peak on each ion-induced spectrum (indicated by the letter a on Figs. 1–4) occurs also under electron bombardment and is well-known to be a $M_{23}M_{45}M_{45}$ transition in the target metal. At around 216 eV there is a broad peak which is observed under Ar $^+$ bombardment, but not for Kr $^+$ or electron impact. This peak is at the position expected for LMM transitions in Argon; the breadth will be explained later in terms of a Doppler effect due to the motion of the Argon projectiles. Between these two peaks there is a variety of additional structure particularly for Kr $^+$ on Cr and Ar $^+$ on Fe. These ion-induced spectra were independent of whether the surface was cleaned and analyzed with the same inert-gas ions or cleaned with one ion species and analyzed with the other. No time-dependent effects were observed once the surface was clean although on a dirty surface the metal $M_{23}M_{45}M_{45}$ peak was less pronounced than on a clean surface. The relative sizes of the various Auger peaks was independent of beam intensity, beam focusing, and angle of incidence on the target. We are, therefore, confident that the various peaks are not artifacts of the apparatus nor of of the CMA.

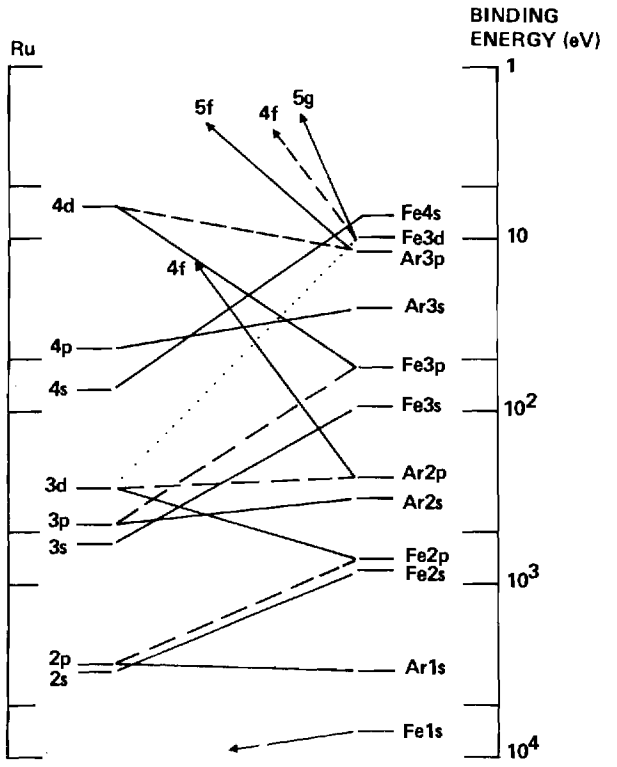

FIG. 5. Correlation diagram for Ar $^+$ + Fe collisions.

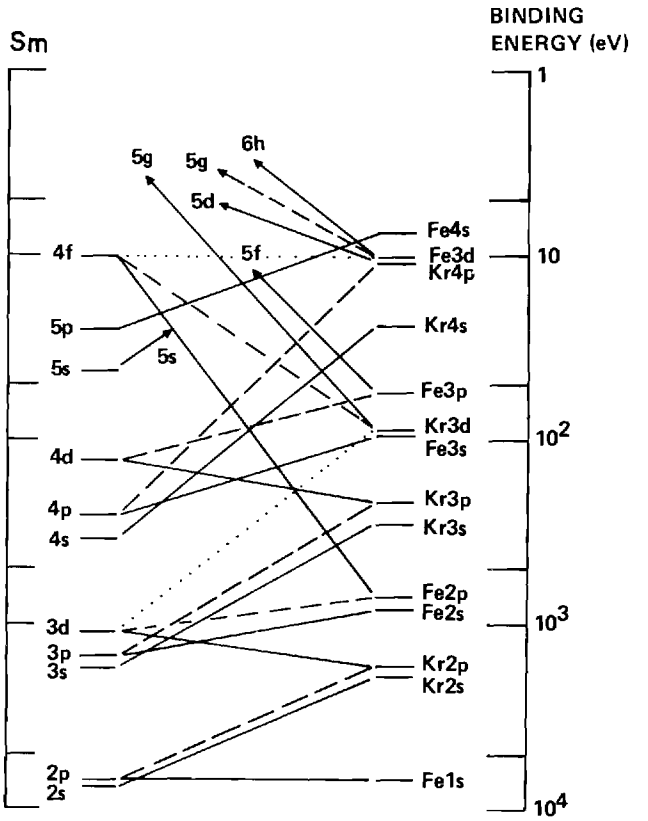

FIG. 6. Correlation diagram for Kr $^+$ + Fe collisions.

With some uncertainty in the beam current density distribution and detection sensitivity over the beam spot, it is not possible to measure absolutely the intensity of the various features. It is however, of interest to measure the relative intensity of the features utilizing fixed ion beam and detection conditions. For this purpose we define intensity as the peak-to-peak height of an Auger feature. In Table I we show the relative intensities of the metal $M_{23}M_{45}M_{45}$ peak and Ar $L_{23}MM$ peak for Ar $^+$ on Cr, Mn, Fe, and Co and the $L_{23}MM$ peak of Si for Ar $^+$ on Si; the values for Cr are set to unity.

IV. DISCUSSION

In Figs. 5 and 6 we show the Fe-Kr and Fe-Ar correlation diagrams drawn according to the prescriptions of Barat

and Lichten[19]; the diagrams for the other target cases are approximately the same and have not been drawn here. Figure 5 shows immediately that strong promotions should occur from the $2p$ shell of Ar leading to LMM lines of Argon. This is in fact seen in Figs. 1–4 as the broad peak at about 216 eV. From Fig. 6 we would expect no promotions from the $2p$ shell of Kr so explaining the absence of a Krypton LMM or LNN transition in the observed spectra. From both Figs. 5 and 6 one would expect promotions from the $3p$ shell of the metal leading to $M_{23}M_{45}M_{45}$ Auger electrons. These are observed as the lowest-energy peak in the ion-induced spectra of Figs. 1–4 and are also seen in the electron-induced spectra. Promotion of the metal $3p$ electron can occur also in symmetric collisions (e.g., Fe + Fe) in the collision cascade.

A. Metal $M_{23}M_{45}M_{45}$ transitions

These are the lowest-energy peaks, visible in all the spectra. The are indicated by the letter a on Figs. 1–4. The ion-induced Auger peaks show an increase in energy of about 1.7 eV over the corresponding peaks due to electron impact, although the width (measured as the energy difference between positive and negative excursions) is similar. The excitation event is caused by a collision between heavy particles resulting in substantial energy transfer to the excited atom. This motion of the species which emits the Auger electron may give rise to shifts of the Auger line. If the excited species is ejected out of the solid, the emitted line will be that of an isolated atom. Using the solid-state correction of Larkin[22] and allowing for the work function, this should lower the Auger line energy for the $3d$ transition metals by about 4.5 ± 2 eV. This is not consistent with our observations which show an increase in Auger line energy. Auger electrons emitted by atoms ejected out of the target will also exhibit a Doppler shift and for the configuration of the present experiment, the majority of sputtered atoms will move towards the observer causing an increase in the observed Auger line energy. This would produce a shift in the observed direction, but we would require the ejected particle energies to be of the order of 2 keV or more to explain the magnitude of the shift, calculated by the formula given by Dahl *et al.*,[23] which seems to be unreasonably high. We are, therefore, unable to offer any convincing explanation of the small energy shift of the metal $M_{23}M_{45}M_{45}$ lines.

Table I shows that the $M_{23}M_{45}M_{45}$ line intensity varies rapidly through the transition-metal series and is considerably smaller than the LMM intensity for a light element such as Si.

B. Metal $M_1M_{45}M_{45}$ transitions

Peaks seen weakly at 64, 74, 82, and 90 eV in Cr, Mn, Fe, and Co, respectively, are[24] the metal $M_1M_{45}M_{45}$ Auger transitions; in Figs. 1–4 they are indicated by the letter b. According to the promotion diagram of Fig. 5 the metal $3s$ level should not be ionized by the direct projectile-target collision. Some more complicated event or sequence of events is taking place. Possibly a target atom recoiling from a projectile-target collision with a $3p$ vacancy collides subsequently with a further target atom causing the vacancy to be transferred to a $3s$ level.

C. Ar LMM transitions

The argon $L_{23}M_{23}M_{23}$ peak lying at about 216 eV in Figs. 1–4 is much broader than one would expect from an isolated stationary atom. We propose that the principal source of such electrons is Ar^+ ions scattered out of the surface and that the line width and shift is due to the Doppler effect related to the recoil speeds and directions of the Ar^+ ions. Figure 7 shows the Auger spectrum induced by Ar^+ impact on Fe for a variety of projectile energies from 20 to 200 keV; the angle of incidence in this case is 65° from the target surface normal. The negative excursion of the line shifts progressively to higher energies as projectile energy is increased; this is to be expected if the Auger electrons come primarily from Ar^+ ions scattered towards the observer and the average recoil energy increases with projectile energy. The most satisfactory method of confirming this contention would be to compute the line shape and compare to the experiment. This is not readily possible due to the complicated annular geometry of the CMA and the lack of detailed information on energy distributions of scattered Ar^+ ions. As an alternative we shall perform a simple calculation of the Doppler shift expected for recoils into a somewhat arbitrar-

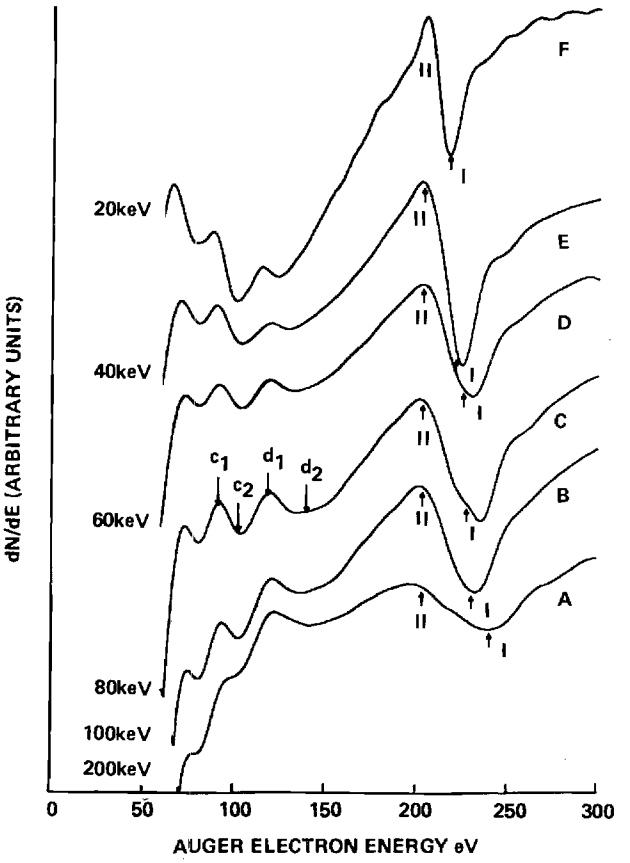

FIG. 7. Auger spectra induced by Ar^+ impact on Fe at energies from 20 to 200 keV. The various indicated features are identified in the text.

ily chosen direction and demonstrate that this is consistent with the progressive change in line shape.

To perform the calculation we consider the case of Ar^+ ions scattered specularly from the surface; this should represent a direction where a large flux of projectiles will occur. We further consider only those Auger electrons emitted in the plane of the projectile and recoil beams. The scattered Ar^+ ion energy is calculated from conservation of energy and momentum in a biparticle $Ar^+ + Fe$ collision on the surface. The Doppler shift is calculated from the formula by Dahl *et al.*[23] An Auger $L_{23}M_{23}M_{23}$ line from a stationary atom will have[25] a group of lines between 203 and 206 eV which in the derivative mode of recording spectra with our CMA will produce a single peak with a positive excursion at 203 eV and a negative excursion at 206 eV. We take the calculated shift obtained by the prescription given above and simply add it to 206 eV to provide a prediction of how the negative excursion should vary with projectile energy; this calculated energy is designated by the symbol I on Fig. 7. On this simple model there should be no downward shift of Auger electron energy since we include no projectiles scattered away from the observer; the positive excursion should therefore remain invariant with projectile energy at the stationary atom value of 203 eV, and this is shown by the symbol II on Fig. 7. The positions of points I and II evaluated in this manner do in fact agree very well with the position of the negative and positive excursions, confirming that the changes in peak position and width are consistent with the Doppler effect. It is also clear that in the limit as projectile energy tends to zero the argon line position extrapolates to the value expected for a free Ar^+ ion. We offer no definite explanation of the weak structure seen on the negative excursion of the argon line for 60- and 80-keV impacts. We do note that the backscattered energy spectrum for Ar^+ ions on polycrystalline materials does show a broad continuum with a sharp peak superimposed due to surface scattering.[26] If recoils with L-shell vacancies have such an energy distribution, the Doppler-broadened line shape of the emitted Auger electrons will have a double-peak structure on the negative excursion.

The lifetime of the argon L_{23} vacancy is estimated by McGuire[27] to be 3.5×10^{-15} sec. Thus for an argon ion with a speed of 2.2×10^{7} cm sec^{-1} (10-keV energy) the decay length is 7.7 Å. Recoils with low energy will therefore frequently undergo the Auger decay event while still interacting with the metal surface. Inevitably this will cause some shift or broadening of the emitted Auger line, further adding to the complexity of the line shape.

The data in Table I shows that the cross section for excitation of the argon Auger line decreases rapidly with increasing atomic number. This in accord with the results found at lower energies.[13,28]

D. Kr Auger lines

According to the promotion diagram of Fig. 6 one would have expected formation of $3d$ vacancies in Kr followed by emission of $M_{45}NN$ Auger electrons at 63 eV.[24] No such line is observed.

The 97-eV line in the $Kr^+ + Cr$ spectrum (Fig. 1) has an energy corresponding to that expected for a $M_3M_{45}N_{23}$ transition in Kr.[24] According to Coghlan and Clausing[24] this should be the most intense line resulting from a $3p$ vacancy. The line width (about 10 eV) is consistent with the Doppler broadening to be expected if the krypton atom is recoiling from the target. It is, however, puzzling that this line does not occur in the case of the other targets. Moreover, according to Fig. 6 the $3p$ vacancy in Kr should not occur due to a single promotion in a Kr^+ collision with a target atom. We consequently regard the identification of this line as only tentative and offer no explanation as to why it occurs only for Cr targets.

Discussion of the krypton spectrum in terms of the correlation diagram of Fig. 6 is probably inadequate. Many of the curve crossings shown in Fig. 6 will be avoided; this occurs specifically when the two intersecting levels have the same angular momentum and parity.[29] Thus the $5g\ \sigma$ level (connecting Kr $3d$ to the $5g$ state of the united atom) will not cross the $4s\ \sigma$ level (connecting Kr $4s$ to the $4s$ state of the united atom). Consequently, the apparently strong $5g$ promotion shown in Fig. 6 will not occur and vacancies will not appear in the $3d$ level of Kr. This may explain the absence of the $M_{45}NN$ transitions. We also note that the whole concept of "crossing" is questionable when the subshell splitting is comparable with the promotion energy,[29] a situation which certainly holds for the M and N shells of the projectile and target.

E. Other features

In the Ar^+ ion induced spectra there are a number of weak features in the 90–200-eV region that cannot be identified as either metal or rare-gas Auger lines. Care was taken to ensure that they were not spurious or impurity related. Movement of these peaks with sample bias showed that they were not an artifact of the beam or of its interaction with, for example, the CMA aperture. They did not result from contaminants since they were independent of the surface condition after initial cleaning. Moreover, the only element with an Auger line close to our observed peaks is phosphorus, which was not detected in the electron-induced Auger spectrum. Deliberately implanting enough phosphorus to be detectable in the electron-induced Auger spectrum did not effect the ion-induced spectrum.

It is impossible that the extra features are interatomic Auger peaks resulting from transitions between the bombarding and target ions. In this type of transition a core hole on one atom is filled by an electron either from that atom or from a neighboring atom, with the ejection of an Auger electron from the neighboring atom. Thus one obtains transitions of the type $K_AM_BM_B$ or $K_AM_AM_B$, where K_A, K_B, etc., are energy levels on the atoms A and B. Transitions of this type have been seen in a number of systems.[30,31] The interatomic transition rate depends on the spatial overlap of the initial hole state (K_A) and the annihilating electron state (M_A or M_B), as well as the initial state of the ejected electron and its continuum wave function.

When two atoms collide, the spatial overlap of different energy levels is greatly enhanced over the overlap in an alloy or compound. To create an Ar $2p$ hole in an Ar-Fe collision, for example, the nuclear separation must be less than about[28] 0.2 Å. This would make possible a large number of interatomic transitions which cannot usually occur in alloys or compounds.

From Figs. 5 and 6 it can be seen that the most readily ionized core levels of the projectile are the Ar $2p$, Kr $3d$, and possibly Kr $3p$. Thus, to account for the peaks we observe, any interatomic transition must involve a core hole in one of these levels. Further, the ejected electron will probably come from a delocalized orbital such as Fe $3d$ or $4s$ or an orbital which tends to become delocalized during the collision such as Fe $3p$, Ar $3p$, Kr $3p$, or Kr $4p$. There are a large number of transitions of the type Ar (L_{23}) Metal (MM) and Kr (M_3) Metal (MM) which would produce Auger electrons in the energy range under consideration. Allowing for the resolution of the analyzer and possible small Doppler broadening effects, most of these transitions would not be resolved. It is also not possible to determine *a priori* which of the many possible transitions are the most likely to occur. To illustrate that the interatomic transitions can provide an explanation of the observed features we shall concentrate on the case of Ar^+ colliding with Fe. Figure 7 shows the collisionally induced Auger spectrum for this case as a function of projectile energy. There are two distinct lines indicated as a c and d, which lie well below the Ar LMM Auger group and do not appear in the electron-induced spectrum of the target material (see Fig. 3).

Peak c extends from a positive excursion at c_1 to a negative excursion at c_2. The width (measured as energy $E_{c_1} - E_{c_2}$) decreases slightly from 13 to 6 eV as the projectile energy increases from 20 to 200 keV. We ascribe this peak to an Ar (L_{23}) Fe (M_1, M_{23}) transition; from the solid-state binding energies of Coghlan and Clausing[24] we would estimate the energy of this transition to be 91 eV which is in good agreement with the observed peak position. An interatomic transition will involve perturbed energy levels of the colliding partners. Furthermore, the energy of the emitted electron will be depressed due to its interaction with the potential of the other atom; this causes a depression and broadening of the emitted line known as the "Berry" effect.[23] This line broadening ΔE_B for a projectile of mass M (amu) with an energy T_i (keV) interacting with a second atom of charge ne and having a core-hole lifetime of τ sec is given by[23]

$$\Delta E_B = 1.07\, b = 1.07 \frac{n 3.30 \times 10^{-15}}{\tau} \left(\frac{M}{T_i}\right)^{1/2} \text{eV}. \quad (1)$$

Clearly the line width decreases with increasing projectile energy, in accordance with the observed behavior of line c. If we plot the line width as a function of $T_i^{-1/2}$ and n is taken as unity, then we derive an effective value of τ of about 3.3×10^{-16} sec. In this time a 20-keV Ar^+ ion will move only about 1 Å, and a 200-keV Ar^+ ion only about 3 Å. It is therefore reasonable to argue that the decay of the Ar L_{23} vacancy occurs while the projectile interacts with the target atom and therefore an interatomic transition is possible. This lifetime is, of course, and order of magnitude shorter than that of an isolated argon atom.[27] However, it is known that the interatomic transitions can greatly reduce hole lifetimes[30] and that the lifetime of L_{23}, shell vacancies are reduced by an order of magnitude when in a matrix.[32] Thus our lifetime estimate is not unreasonable. There is no appreciable Doppler effect because the source of the monitored electron is an Fe atom which is either at rest in the matrix or recoils with a relatively low velocity. It is to be noted that as projectile energy increases to 200 keV the magnitude of this peak becomes small compared with the other features. This is to be expected since with the increased projectile speed the time of interaction between projectile and target will decrease, so reducing the probability of an interatomic transition.

Peak d has a width ($E_{d_1} - E_{d_2}$) which increases significantly with increasing projectile energy. We ascribe this peak to a transition of the type Ar (L_{23}) Fe (M_1) Ar (M_{23}) whose energy from a stationary system is about 135 eV.[24] The increase of width with projectile energy is similar to that of the argon line designated I and II on Fig. 7. This shows that the width change is again a Doppler effect due to the fact that the observed electron comes from the projectile Ar which is in motion.

There are in fact at least eight interatomic transitions for Ar^+ projectiles in the energy region 90–200 eV and we would not claim that the above discussion provides positive identification of peaks c and d. We do, however, conclude that these peaks are due to interatomic transitions and that the electron in peak c comes from an Fe atom in the matrix, and for peak d the electron comes from a moving projectile. We have also indicated the position of the corresponding transitions for Cr, Mn, Fe, and Co targets on Figs. 1–4 and there is a correspondence between observed features and the predicted line position particularly for Mn, Fe, and Co.

In the case of krypton impact there are few distinct features other than the metal $M_{23}M_{45}M_{45}$ peak. In the case of Kr^+ on Cr, there is a distinct line at 97 eV which we have ascribed to the $M_{23}M_{45}M_{45}$ transition in krypton, meaning that in this case there are inner-shell vacancies produced in the projectile. The second subsidiary (peak e on Fig. 1) could be an Kr (M_3) Cr ($M_{23}M_{23}$) peak for which we would calculate[24] an energy of 124 eV in essential agreement with the observed peak position. In the remaining Kr^+ impact spectra there is no definite identification of krypton peaks and no definite subsidiary structures. We would conclude that vacancy formation in the krypton has a small cross section and therefore interatomic lines (which involve the projectile vacancy) are not observed.

CONCLUSIONS

The Auger spectra induced by impact of Ar^+ and Kr^+ ions on Cr, Mn, Fe, and Co differ markedly from the spectra induced by electron impact on these same metals. The only common feature is excitation of the metal $M_1M_{45}M_{45}$ and $M_{23}M_{45}M_{45}$ lines which lie at quite low energies. Ar^+ impact also produces the Doppler-broadened

$L_{23}M_{45}M_{45}$ line of argon whose width and shape is consistent with the primary source of electrons being projectiles scattered out of the surface. Formation of the L_{23} vacancy is consistent with electron promotion during the interaction of the projectile with a target atom. With the possible exception of a $M_{23}M_{45}M_{45}$ line in $Kr^+ + Cr$ collisions we identify no sizeable spectral features from krypton induced by Kr^+ impact on the various targets. For Ar^+ impact there are a variety of additional features in the energy region 90–200 eV which cannot be identified as due either to the target system or to the projectile system. We propose that these lines are interatomic transitions where the vacancy created in the inner shell of a projectile by the promotion mechanism is filled by a transition involving electrons of the target atom.

ACKNOWLEDGMENT

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Abstract of Review Article accepted for
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FORMATION OF EXCITED STATES BY ION IMPACT ON SURFACES*

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Abstract - Impact of energetic ions on surfaces gives rise to a variety of excited states in the sputtered particles, in the reflected projectiles and sometimes of molecular species bound to the surface. Where the outer shell of the system is excited the state will normally decay with emission of optical photons that may be detected with conventional spectroscopy. Where there are vacancies in the inner shells the species may be detected by subsequent emission of Auger electrons or x-rays. The review provides a comprehensive catalogue of the available data and attempts to correlate the various observations. Optical emissions from sputtered and recoil particles are strongly influenced by radiationless de-excitation processes and this is incorporated into models that describe both line shape and line intensity. There is, however, no well developed description of how the excited states are formed. Thermal excitation models that describe excitation in terms of a Local Thermodynamic Equilibrium plasma are shown to be poorly founded. Alternative models ascribing excitation to bi-particle collision events have not yet been quantitatively tested. Inner shell excitation certainly appears to be governed by electron promotion events in the transient quasi-molecule formed by a projectile and target atom. We review briefly the possible applications of ion induced optical emission to the analysis of surface composition.

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