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"Semi-Auger" Processes in L_{23} Emission in Ar and KCl

J. W. Cooper and R. E. LaVilla
National Bureau of Standards, Washington, D. C. 20234
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X-ray emission studies in Ar and KCl due to formation of an L_{23} vacancy reveal a low-energy satellite below the main emission peak. Comparison with other data on related processes indicates that this satellite is due to two-electron effects (configuration interaction) in the final state of the emission process.

In this Letter we wish to report direct evidence of a two-electron process in L_{23} emission which corresponds to simultaneous filling of an inner-shell hole and excitation of a valence-shell electron with emission of a single photon. This process, which would produce a low-energy satellite approximately 10 eV below the main L_{23}-M_1 emission peak, has been observed previously[1-3] in K and Cl spectra. While processes of this type have been postulated earlier,[4,5] it has been impossible to demonstrate conclusively that they are in fact occurring in experiments of this type.[1-3] The use of argon gas in our experiment makes it possible to rule out double vacancies in the initial state as an explanation of the observed low-energy spectral feature. It also makes possible a definitive interpretation of the emission results in terms of the known spectroscopic levels of Ar II. Evidence for a similar process in K-shell emission of Al, Si, and S involving two-electron processes in the L_{23} subshell has recently been reported.[6] However, the intensities of these K-shell emission features[6] represented only a small fraction (<1 %) of the parent line, whereas in the L_{23} emission reported here the effects are considerably larger (of the order of 10 % of the parent line).

Emission spectra were obtained using a single-crystal Bragg spectrometer with a Langmuir-Blodgett type lead myristate analyzer. Resolution of the analyzing crystal (~2 eV) is unknown. The resolution as limited by 0.4° Soller slits varied with wavelength from about 1.25 eV (at potassium L_{23}) to about 0.21 eV (at Cl L_{23}). Radiation was detected with a flowing-gas proportional counter followed by conventional electronic data logging, while step-scanning. Excitation was provided via a Pierce-type electron gun operating at 10 kV with a current of 100 mA in the case of argon and 0.05 mA for KCl spectra.[7] For the argon measurements the target atoms consisted of a continuous gas flow through the system. The KCl L_{23} spectra were obtained from a single crystal of KCl attached to a nickel strip with silver conducting epoxy. Ni $L\alpha_{1,2}$ radiation in third through fifth orders and C $K\alpha$ from graphite were used to calibrate the energy scale. Further experimental details will be presented elsewhere.

Emission spectra corresponding to Cl, Ar, and K are shown in Figs. 1(a), 1(b), and 1(c) respectively. The potassium L_{23} emission spectra in Fig. 1(c) is located on the tail of the carbon $K\alpha$ emission which comes from pump oil deposited on the specimen. Figure 1 shows, in addition to an unresolved L_{23} doublet (the large peak), an additional structure lying approximately 6, 11, and 14 eV below the main peak in Cl, Ar, and K, respectively. The separation of the low-energy peak from the main peak in KCl is in agreement with previous measurements.[2,3]

The interpretation of the low-energy peaks in Fig. 1 as a "semi-Auger" process requires that all other possibilities be ruled out. Alternative possibilities include the following: (1) Excitation of L_1 rather than L_{23} may occur followed by an L_1-L_{23},M Coster-Kronig process leading to L_{23} and M vacancies in ions of higher charge. (2) Two-electron excitations may occur in the excitation process, i.e., the formation of L_{23} single vacancies may be accompanied by a fraction of ions in excited or doubly ionized states due to electron "shakeoff."[8]

Both of these possibilities can be ruled out in the case of argon by energetic considerations.

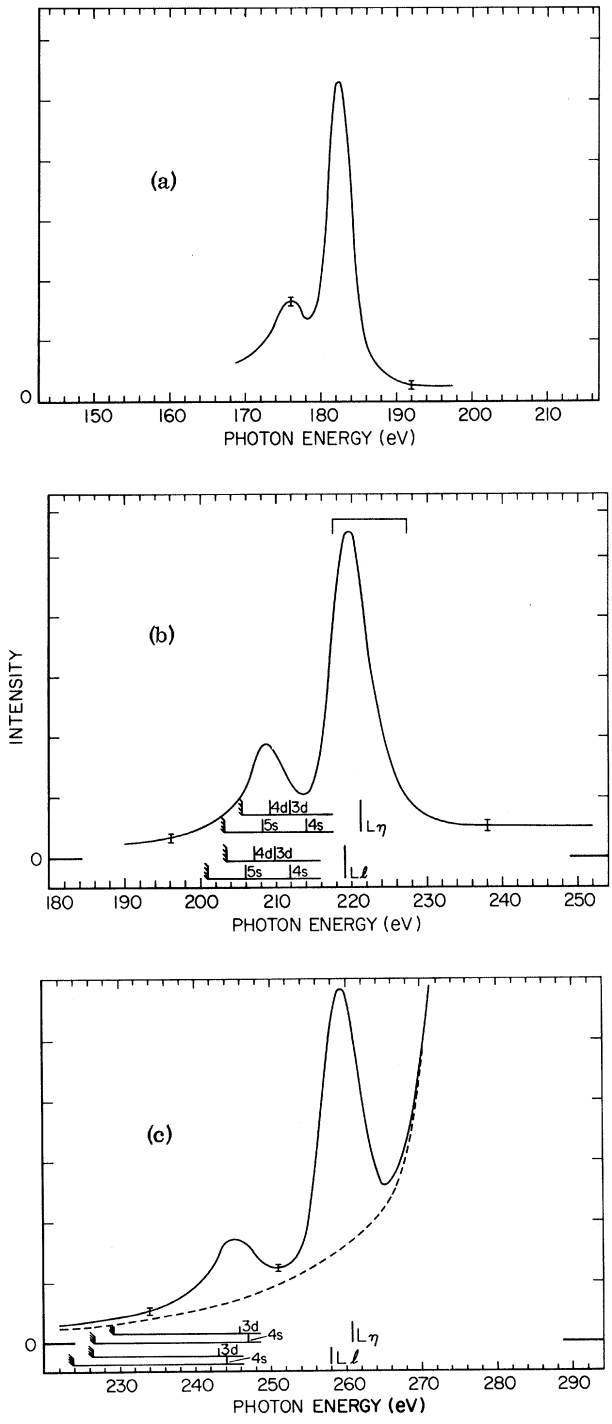

FIG. 1. The emission spectra in the L_{23} region for (a) Cl in KCl, (b) argon gas, and (c) K in KCl. $L\eta$ and Ll are the L_{23}-M_1 doublet. Error bars indicate an estimated range of intensity variations in repeated experiments. The bracket at the top of (b) shows the band of energies that represent contributions from double vacancy states. The dashed line in (c) is the estimated tail of the C $K\alpha$ emission. Beneath the spectra in (b) and (c) are plotted the positions and limits of the ^2S levels taken from Refs. 11 and 17.

First, we know, as the result of recent work,[9,10] that the L_{23} levels in argon lie 248.4 and 250.6 eV above the ground state of Ar I. The known position of the $3s3p^6$ level in Ar II above the ground state of Ar I is 29.23 eV.[11] Therefore, the energy of transitions L_{23}-M_1 in Ar II must be 219.2 and 221.4 eV. The agreement of these values with the energy of the main peak in Fig. 1(b) identifies the main peak as an unresolved L_{23}-M_1 doublet in Ar II.

Secondly, the recent work of Mehlhorn[12] and of Mehlhorn and Stalherm[13] on L_1 and L_{23} Auger processes in argon rules out (1) as a possibility for the low-energy peak of Fig. 1(b). The relevant data are summarized in Table I. This table shows that if a L_{23},M_{23} double vacancy is formed, emission will occur in a band of energies between 217.6 and 227.4 eV and may, in fact, contribute substantially to the strength of the main peak. Since emissions from L_{23},M_1 double vacancies will occur at even higher energies, such transitions cannot be responsible for the low-energy satellite in Fig. 1(b). This argument also rules out (2), insofar as double ionization occurs via shakeoff, since the initial states of the radiative process will be the same whether the L_{23}, M_{23} double vacancy is formed by a Coster-Kronig or shakeoff process. Excitation without ionization by (2) is not ruled out by the above argument. However, it is unlikely that such a process makes an appreciable contribution to the low-energy satellite in Fig. 1 since the initial and final

Table I. Energies of initial and final states of Ar III which could produce transitions via a radiative process. Energies (in eV) are relative to the ground-state energy of Ar I and have been obtained from the data of Refs. 16 and 13 assuming 326.5, 250.6, and 248.4 eV for the Ar L_1, L_2, and L_3 binding energies, respectively. The range of energies of possible transitions lies between 217.6 and 227.4 eV as shown in Fig. 1(b).

Initial state $(2p^5 3s^2 3p^5)$ $^{1,3}L_j$		Final state $(2p^6 3s 3p^5)$ $^{1,3}L_j$	
$^1S_0$	285.1	$^1P_1$	61.3
$^1D_2$	283.5	$^3P_0$	57.8
$^3P_1$	282.7	$^3P_1$	57.7
$^3P_0$	282.2	$^3P_2$	57.5
$^3D_1$	281.5		
$^3P_2$	281.4		
$^3S_1$	280.6		
$^3D_2$	280.1		
$^3D_3$	279.2		
$^1P_1$	278.9		

states in a singly ionized excited ion will have approximately the same energy difference as doubly ionized states. In addition, the probability of shakeoff in L_{23} excitation of argon, approximately 1-2%, calculated in sudden approximation,[14] is too low to account for the relatively large intensity (~10%) of the low-energy satellite shown in Fig. 1.

The above analysis, in addition to eliminating double excitation as a process contributing to emission of the low-energy satellite, also suggests why the L_{23} doublet is not readily resolved. Processes 1 and 2 are about as likely to occur at the bombarding energies used here as single L_{23} vacancy formation, as has recently been reported.[15] Theoretical estimates of process 2 are also large.[16] Therefore, a large part of the intensity of the main L_{23} emission is probably due to double vacancy formation. This is suggested in the early measurements on Cl by Siegbahn.[5]

The presence of low-energy satellites in L_{23} emission can be attributed to strong mixing of the final state configuration $3s3p^6\,{}^2S$ with states in which one $3p^6$ electron is removed and another excited. The even levels which will mix are $3s^23p^4ns\,{}^2S$ and $3s^23p^4nd\,{}^2S$. Analysis of the Ar II spectra[17] indicates that $3s3p^6\,{}^2S$ mixes strongly with $3s^23p^4nd\,{}^2S$, but weakly with $3s^23p^4ns\,{}^2S$. Additional experimental evidence for this effect is obtained from the long lifetimes of radiative decays from the $3s3p^6\,{}^2S$ state.[18] Qualitative estimates of the strengths of these interactions have been made by configuration-interaction calculations in Ar II.[19]

The above optical data appear to indicate that the main intensity of the low-energy satellites shown in Fig. 1 is due to the strong mixing of $3s3p^6\,{}^2S$ and $3s^23p^4nd\,{}^2S$ configurations. In Figs. 1(b) and 1(c) we have plotted the positions of all known ^2S levels in Ar II and K III relative to $3s3p^6\,{}^2S$. From the positions of these levels it appears that both $3s^23p^43d\,{}^2S$ and $3s3p^44d\,{}^2S$ states contribute to the satellite intensity whereas in K III the major contribution is for $3s^23p^43d\,{}^2S$. This is not surprising since when strong configuration mixing occurs the intensity sharing of radiative processes depends on the details of the mixing.[20]

The corresponding energy levels for Cl I are not known so that the same type of analysis for the L_{23} emission from the valence band of KCl cannot be made. However, the small energy separation between the main emission band and the satellite (6 eV) makes it appear probable that the same type of argument will apply to the Cl L_{23} emission structure.

The physical picture that emerges from the above analysis is that the L_{23} hole can be filled either by a single-electron process, $2p^53s^23p^6\,{}^3P_{3/2,1/2}$-$2p^63s3p^6\,{}^2S$, or by a double-electron process in which one M_{23} electron fills the L_{23} vacancy and another electron is excited in order to conserve angular momentum.[21] The similar spectra obtained for L_{23} emission in both the K and Cl emission in KCl indicate that this effect is also important in L_{23} emission involving solids. Its relative importance for elements of higher or lower Z and for different states of chemical combination remains to be investigated.

Finally, it is possible that the final states of the radiative process may involve configurations in which an M_1 vacancy is formed and a M_{23} electron excited. Since spectroscopic evidence of these states is not available we have calculated the energy of the center of gravity[22] of the configuration $3s3p^54p\,{}^2S$ in Ar II which lies 19 eV above the energy of $3s3p^6\,{}^2S$. This result indicates that the extreme low-energy tail of the satellite in Fig. 1 may in fact be due to such states. From a configuration-interaction standpoint this is understandable. Configurations such as $3s3p^5np\,{}^2S$ will mix to a certain extent with $3s3p^6\,{}^2S$ and $3s^23p^4nd\,{}^2S$, but in general will lie higher in energy.

A more detailed study of this effect requires further experiments with higher resolution in order to separate, if possible,[21] the various components of the emitted radiation, and more sophisticated theoretical calculations of the configuration mixing in the final states in order to predict the relative intensities of the various spectral components.

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[22]These calculations were performed using the Hartree-Fock code of Dr. C. Froese. We would like to thank Dr. J. Tech of the National Bureau of Standards for performing this calculation and Dr. T. Carlson of the Oak Ridge National Laboratory for performing similar calculations on states of Ar III and K III which were useful in our analysis of the effects of Coster-Kronig processes and shakeoff on our results.

Order-Disorder Phase Transition in Binary Alloys–Coherent Potential Approximation*

E-Ni Foo† and H. Amar
Department of Physics, Temple University, Philadelphia, Pennsylvania 19122
(Received 10 August 1970)

The electronic density of states of a one-dimensional AB model alloy with long-range order is calculated in the coherent potential approximation. Impurity states are found inside the energy gap and the energy gap disappears long before the alloy becomes completely disordered. The temperature-dependent long-range order exhibits a first-order order-disorder phase transition which causes a discontinuity in the electronic density of states at the middle of the energy gap at the critical temperature T_c.

Disordered systems and, more specially, disordered alloys constitute a central problem in modern statistical physics. While the electronic density of states (EDS)[1-7] and the atomic correlation function (ACF)[8,9] of alloys have been intensively studied in recent years by many authors, their relationship has received relatively little attention. The EDS has been calculated only where the ACF vanishes (completely disordered alloys).[1-6] Attempts to include a finite pair correlation have been so far unsatisfactory.[7] It is known, however, that the interatomic potential which determines the ACF depends on the overlap of electron distributions from the various sites and the EDS also depends on its environment (ACF). Since the ACF and the EDS are correlated, they should be determined in a self-consistent manner. In this paper, we use the powerful coherent potential approximation (CPA) of Soven[1] to calculate the EDS from a known ACF. Then the value of the ACF is so adjusted that the free energy of the alloys is a minimum, and the EDS and ACF are determined as functions of temperature T. For an alloy with a half-filled band, the EDS at the Fermi surface increases with T and has a discontinuity at a critical temperature T_c.

Soven's single-site CPA is modified for a partially ordered alloy with long-range order (LRO) η. The CPA is developed in the framework of multiple-scattering theory introduced by Lax.[10] In this approximation, the electron is regarded as propagating in an effective medium. The effective Hamiltonian retains the full crystal symmetry and has a coherent potential (CP) at each site. Here the CP is a complex quantity describ-