$L_{2,3}M_{4,5}M_{4,5}$ Auger spectra of free Ga and Ge atoms

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The $L_{2,3}M_{4,5}M_{4,5}$ Auger-electron spectra of Ga and Ge have been measured for the first time from their atomic vapors with use of electron-impact excitation. The spectra have also been calculated theoretically by taking explicitly into account the partially filled outermost shell. The satellite structure arising from doubly ionized initial states has been investigated by calculating relativistically the energies of satellite lines and comparing them with the experimental spectra. The comparison with the solid-state Auger spectra gives for the free-atom—solid energy shifts 19.1 eV for Ga and 18.7 eV for Ge, by using vacuum and Fermi levels as the reference levels for free atoms and solid samples, respectively. These shift values agree well with the estimates calculated by the semiempirical thermochemical model.

I. INTRODUCTION

We have recently studied[1,2] the $L_{2,3}M_{4,5}M_{4,5}$ Auger-electron spectra of free Cu and Zn atoms. It was found that besides the diagram Auger lines also the double vacancy satellite peaks appeared on the low-kinetic-energy sides of the main diagram Auger line groups. The satellite lines associated with the L_2 group partially overlapped the L_3 diagram group, complicating the analysis of that line group. Because the $L_{2,3}$ spin-orbit splitting increases rather rapidly with increasing atomic number it can be expected that this overlap is smaller for Ga and Ge than for Cu and Zn.

The Auger transitions in open-shell configurations with an outer s electron were studied[3] recently by our group. The Auger transitions involving the next inner shell showed clear fine structure due to the coupling of the outer electron with the holes produced in the Auger decay. In this work we continue our efforts to research the influence of the outermost partially filled p shell on the spectrum. The vapor-phase measurements are motivated also by the need of atomic spectra for comparison with solid-state spectra in order to obtain, e.g., reliable values for the free-atom—solid kinetic-energy shifts.

II. EXPERIMENTAL

The Auger spectra have been measured by means of a cylindrical mirror electron spectrometer modified for inductive heating. The analyzer operates at a mean emission angle of 54.5° and no retardation of the Auger electrons before entering the analyzing field was applied. The induction coil as well as the electron gun are located inside the inner cylinder and water-cooled cooling cylinder. The exciting electron beam goes through the vapor oven made of graphite. The typical acceleration voltage in the electron gun was 4 kV and the primary beam current was ~ 1 mA. The analyzing voltage was controlled by a microprocessor and the data were collected into its memory.

The energy calibration of the spectra was achieved by recording simultaneously with the vapor spectra also the Auger spectra of Ar and Ne rare gases. The energy values of 203.50 and 804.46 eV were used for Ar $L_3M_{2,3}M_{2,3}(^1D_2)$ and Ne $KL_{2,3}L_{2,3}(^1D_2)$ lines, respectively.

III. RESULTS AND DISCUSSION

A. Diagram Auger transitions

The original Auger spectra of Ga and Ge are shown in Fig. 1 with adjusted energy scales so that the main peaks coincide. At first sight the spectra look very similar. This was expected because these transitions take place between the core levels for which the influence of outermost

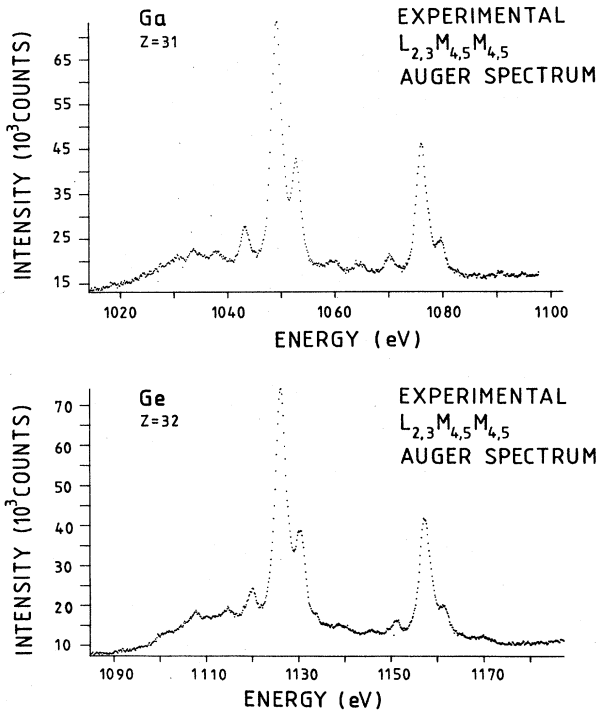

FIG. 1. Experimental $L_{2,3}M_{4,5}M_{4,5}$ Auger-electron spectra of Ga and Ge excited by a 4-kV electron beam.

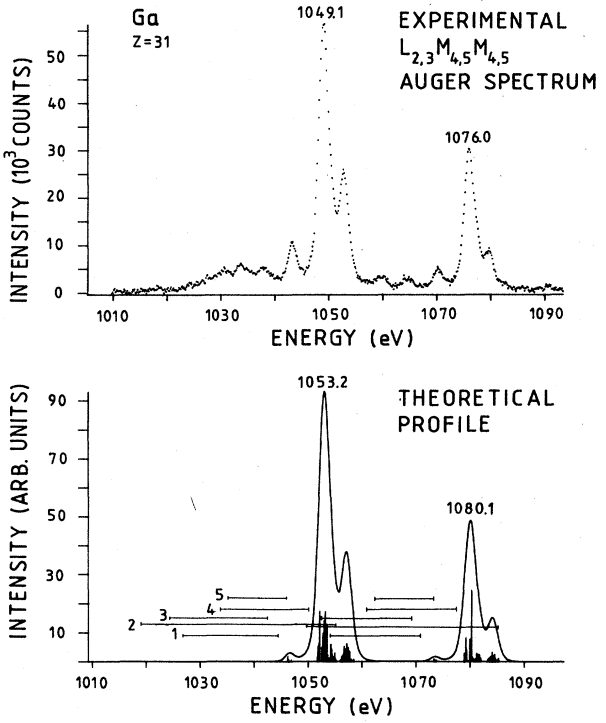

FIG. 2. $L_{2,3}M_{4,5}M_{4,5}$ spectrum of Ga. The upper curve shows the experimental spectrum and the lower curve shows the calculated profile produced by using the open-shell calculation procedure. Horizontal bars represent the following satellite transitions: (1) $2p^5 3s^1 4p^1 \rightarrow 3d^8 3s^1 4p^1$, (2) $2p^5 3p^5 4p^1 \rightarrow 3d^8 3p^5 4p^1$, (3) $2p^5 3d^9 4p^1 \rightarrow 3d^7 4p^1$, (4) $2p^5 4s^1 4p^1 \rightarrow 3d^8 4s^1 4p^1$, and (5) $2p^5 4s^2 \rightarrow 3d^8 4s^2$.

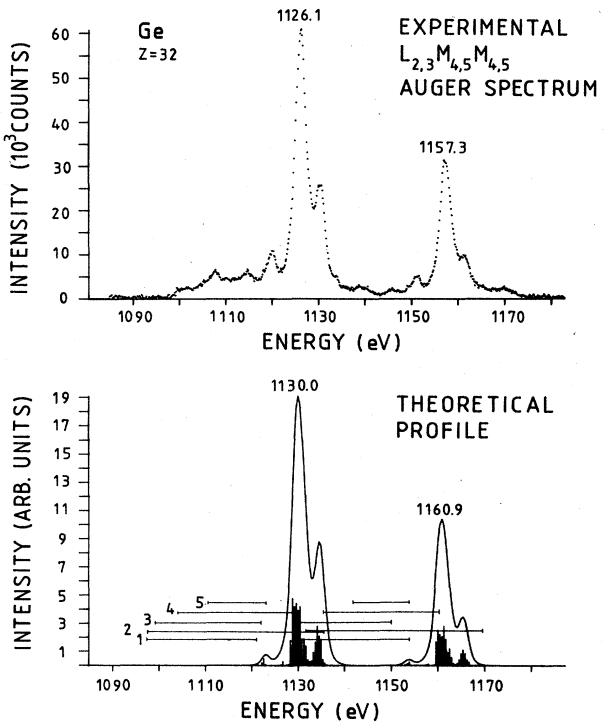

FIG. 3. Experimental and calculated profiles of the $L_{2,3}M_{4,5}M_{4,5}$ transitions of Ge. See the caption of Fig. 2 for details.

$4p$ electrons is not very pronounced. The inherent width of the $3d$ core hole states is rather large, smearing out much of the fine structure arising from the open $4p$ shell.

This finding is nicely demonstrated in Figs. 2 and 3, where the experimental spectra corrected for a smooth background are shown together with the profiles produced by using the calculated energies and transition probabilities. The kinetic energies of main maxima of the Auger spectra are also indicated in Figs. 2 and 3. The method used in the calculations which explicitly takes into account the open-shell structure is described in more detail in Ref. 3. Due to the coupling between the holes of the Auger process and the open outermost shell the number of line components is so high that the decomposition of experimental spectra into components loses its meaning. Therefore we will compare the experimental and calculated Auger profiles.

Comparison between the profiles in Figs. 2 and 3 clearly indicates that Ge, having two outer $4p$ electrons, also contains more lines than Ga, which has only one $4p$ electron. This results in a stronger broadening of the main peaks in the spectrum of Ge compared with the spectrum of Ga. Theory seems to reproduce the observed broadening quite well. The main peak structure, however, remains very similar as foretold above. This is because the daughter levels, caused by the coupling of the outer electrons with the hole states produced by the Auger decay, lie close to their parent levels. This is due to the weak electrostatic interaction between $3d$ and $4p$ electrons.

The relativistically calculated absolute energies of the main peaks (see Figs. 2 and 3) are predicted theoretically to be about 4 eV larger than those found experimentally. This deviation is almost exactly the same as for Cu and Zn.[4]

For the L_3 to L_2 intensity ratios the value 2.1 was obtained from the background-subtracted spectra of Figs. 2 and 3. These intensity ratios agree very well with the statistical ionization-probability ratio in these levels. These show that L_2-L_3X Coster-Kronig processes are not possible for free Ga and Ge atoms, as already found[1,2] for atomic Cu and Zn spectra.

B. Satellite transitions

The double-hole initial-state satellite Auger transitions are created either by a direct double-ionization process or by single ionization in the L_1 level followed by the $L_1L_{2,3}X$ Coster-Kronig process, where X stands for $M_{2,3}$, $M_{4,5}$, N_1 or $N_{2,3}$. Due to the very high number of double-hole initial-state and triple-hole final-state combinations, these satellites appear in the spectra as rather smooth profiles. Instead of discussing individual satellite lines we restrict our consideration to the energy ranges of different satellite transition types.

Energy regions of the satellite transitions calculated with the Dirac-Fock program of Grant *et al.*[5,6] are de-

picted in Figs. 2 and 3. Part of the satellite transitions lie outside the diagram lines but some fall in the same energy regions with the diagram transitions. The spread of the satellite groups seems to increase in going from Ga to Ge, especially in the case of the $L_{2,3}N_1 \rightarrow M_{4,5}M_{4,5}N_1$ transitions. This arises from the coupling of the two (one) $4p$ electrons in the case of Ge (Ga) with the hole states of the satellite transitions.

The increase of the $L_{2,3}$ spin-orbit splitting in going from Zn to Ga to Ge should lead to a smaller overlap of the satellite and diagram line groups. However, the increase in the spread of the satellite transitions due to the open outermost-shell structure compensates the increase in the separation of the L_3 and L_2 diagram line groups. As a result, the overlap does not decrease.

The peak structures of the satellites are not the same for Ga and Ge. No effort to calculate the satellite profiles has been made in this work.

C. Free-atom—solid Auger-energy shifts

Solid-state $L_{2,3}MM$ Auger spectra of Ga and Ge have been studied, e.g., by McGilp and Weightman[7] and by Antonides *et al.*[8] The use of the kinetic energies given by Antonides *et al.*[8] shows that the solid-state Auger energies referred to the Fermi level are 19.1 higher for Ga and 18.7 eV higher for Ge than the corresponding free-atom values referred to the vacuum level. These observed Auger shifts can be compared with calculated values using the semiempirical thermochemical model, which has been found to reproduce the experimental shifts very well.[9,10] This model was used by the authors to calculate shift values at 19.8 eV for Ga and 20.7 eV for Ge in Ref. 9. In these calculations we used pure $(Z+1)$ and $(Z+2)$ approximations for single and double core-ionized species. Very recently Mårtensson *et al.*[10] have shown that these approximations can be slightly improved by using a semiempirically calculated correction term. By using their values, calculated shifts of 18.9 and 19.7 eV are obtained for Ga and Ge, respectively. The agreement between experimental and calculated values is improved so that the calculated shift is 0.2 eV too low for Ga and 1.0 eV too high for Ge. This agreement is very good, taking into account that Ge is not a good metal but a semiconductor and the model, which assumes complete screening of the core holes by the conduction electrons, is actually valid only for metals. The higher deviation in Ge nicely indicates this fact.

ACKNOWLEDGMENTS

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