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Auger transitions in open-shell atoms In and Sn

H. Aksela, T. Mäkipaaso, and S. Aksela
Department of Physics, University of Oulu, SF-90570 Oulu 57, Finland

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$M_{4,5}N_{4,5}N_{4,5}$ Auger transitions in open-shell atoms In and Sn are studied by comparing the calculated profiles with the experimental free-atom spectra. In and Sn atoms have the ground-state electron configurations . . . $4d^{10}5s^25p$ and . . . $4d^{10}5s^25p^2$, respectively. The usefulness of the applied theory to predict the fine structure, which is due to the coupling of the electrons in the $5p$ shell with the electrons involved in the Auger decay, is investigated in going from the closed-shell atom Cd to the open-shell atoms In and Sn.

I. INTRODUCTION

After intensive studies of the Auger spectra of closed-shell atoms (rare gases, alkaline-earth metals, Mg, Zn, Cd, and Hg) during the last years, the interest is now more turning to Auger electron spectra of open-shell atoms. Very few detailed studies of non-closed-shell Auger transitions for single-ionized atoms have been published until now. In order to understand a little better the influence of the partially filled outermost shell on the fine structure of the Auger spectra, we report in this paper a detailed analysis of the $M_{4,5}N_{4,5}N_{4,5}$ spectra of In and Sn atoms.

The ground-state electron configurations of In and Sn are . . . $3d^{10}4s^24p^64d^{10}5s^25p$ and . . . $3d^{10}4s^24p^64d^{10}5s^25p^2$, respectively. The $3d^{-1} \rightarrow 4d^{-2}$ transitions of In and Sn show a rich fine structure due to the coupling of the electrons participating into the Auger decay with the electrons in the outermost partially filled shell. Owing to the variety of the energy levels lying close to each other, a detailed analysis of an open-shell Auger spectrum is very difficult without knowledge of the intensity distribution. In this work we study how the theory predicts the redistribution of the intensity of the parent lines to the daughters. Furthermore, we discuss the influence of this redistribution to the profile of the spectrum and the possibilities to carry out a detailed interpretation of the experimental spectrum.

II. EXPERIMENT

The $M_{4,5}N_{4,5}N_{4,5}$ Auger spectrum of free In atoms was published recently.[1] An assignment of the main peak structure of the spectrum was based on a comparison with optically known final-state energy levels.[2,3]

The $M_{4,5}N_{4,5}N_{4,5}$ spectrum of atomic Sn has not been published earlier. The spectrum has been measured by means of the cylindrical-mirror-type electron spectrometer equipped with the resistance-heated high-temperature furnace.[4] The spectrum was excited by a primary electron beam of 3 kV voltage and 1 mA current. The applied vapor pressure inside the furnace was about 0.1 Pa, corresponding to a temperature of about 1100 °C. The standard pulse-counting method was used applying a microprocessor based spectrometer control and data-collecting system. The Auger electrons were registered without any retardation before analyzer field.

The energy calibration of the spectrum of atomic Sn was

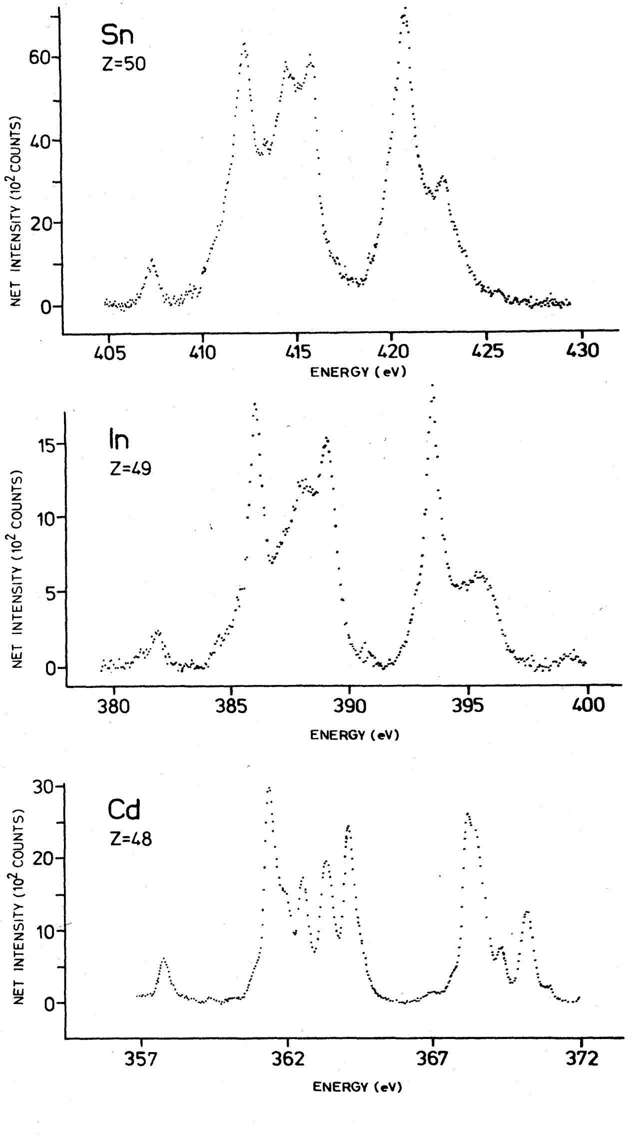

FIG. 1. Experimental $M_{4,5}N_{4,5}N_{4,5}$ Auger electron spectra of Cd, In, and Sn atoms. The spectra of Cd and In are obtained from Refs. 6 and 1, respectively, and the spectrum of Sn is measured in this work. Background subtraction and dispersion correction have been performed in the plotted profiles.

achieved recording simulataneously with the vapor spectrum also the Ar $L_3M_{2,3}M_{2,3}(^1D_2)$ and Ne $KL_{2,3}L_{2,3}(^1D_2)$ lines. The energy values[5] of 203.50 and 804.46 eV were used for these Ar and Ne lines, respectively. The experimental free-atom spectrum of Sn is shown in Fig. 1, together with the atomic spectra of Cd (from Ref. 6) and In (from Ref. 1).

III. DISCUSSION

In order to follow the splitting of the parent lines to the daughters in going from a closed-shell Auger spectrum to open-shell spectra we have first carried out an energy analysis of the $M_{4,5}N_{4,5}N_{4,5}$ spectra for the elements from Cd to Sn. Cd has a closed-shell ground-state electron configuration . . . $3d^{10}4s^24p^64d^{10}5s^2$. The splitting observed in the spectrum is all due to the vacancies produced by the Auger decay. In the spectrum of In we observe extra fine structure due to the coupling of the outer $5p$ electron with the electrons participating into the decay. A drastic increase in the number of the possible energy levels takes place in the case of Sn. The ground-state electron configuration of Sn is . . . $3d^{10}4s^24p^64d^{10}5s^25p^2$. The final-state energy-level structures of the elements Cd to Sn are depicted in Fig. 2. The level which is found to gain most of the intensity in the Auger spectrum is choosen to be the reference level. The drawing is based on the calculations carried out with the multiconfiguration Dirac-Fock program of Grant, Kenzie, and Norrington.[7] The energies of the final-state levels are determined by performing relativistic self-consistent field (SCF) calculations for the doubly ionized atom using single-manifold approach corresponding to nonrelativistic configuration. The energies of Auger transitions are obtained as differences between separately optimized total energies of the singly ionized initial- and doubly ionized final-state levels of the Auger process (the ΔSCF approach).

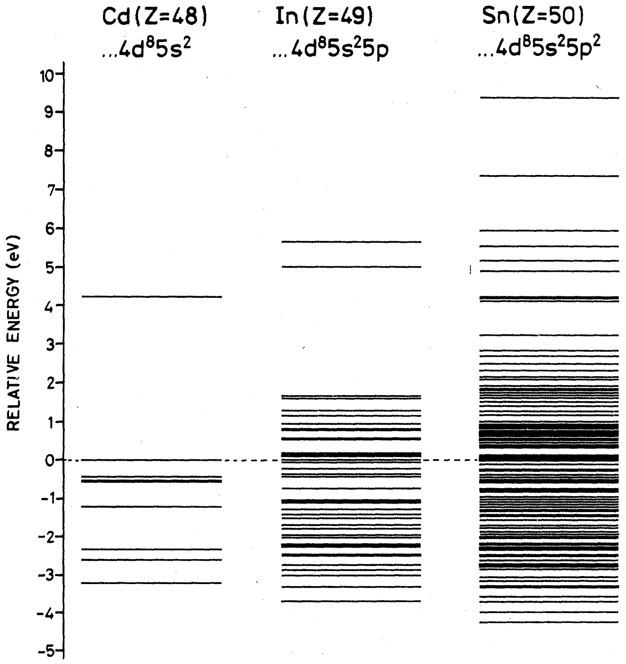

FIG. 2. Final-state energy-level structures of Cd, In, and Sn atoms predicted by the single-manifold Dirac-Fock calculations.

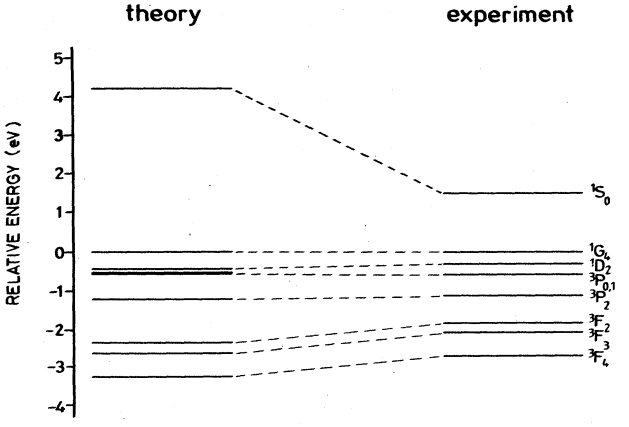

FIG. 3. Comparison between calculated and experimental (Ref. 2) splitting of the . . . $3d^{10}4s^24p^64d^85s^2$ configuration of Cd.

For Cd and In the final-state energy-level structure can be taken from optical data[2,3] and thus a comparison between calculated and experimental energies becomes possible. Figure 3 shows this kind of comparison for the energy splitting relative to the $^1G_4$ level of the $4d^{-2}$ configuration of Cd. For In the experimental splitting shown in Fig. 4 is obtained from In v and corresponds the . . . $4d^85p$ configuration whereas the calculated energy splitting is for the . . . $4d^85s^25p$ configuration of In. The deviations in the energy-level splittings of the . . . $4d^85s^25p$ and . . . $4d^85p$ configurations of In are not, however, expected to be large. According to the Dirac-Fock calculations the two splittings agree within 5%.

An inspection of Fig. 3 shows that the theory clearly overestimates the splitting of the . . . $4d^85s^2$ configuration for Cd. Especially the position of the $^1S_0$ level is poorly es-

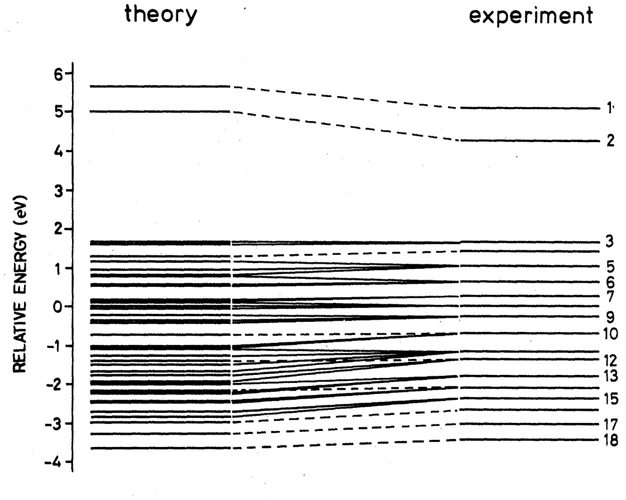

FIG. 4. Comparison between calculated and experimental final-state energy splitting of In. The calculations are carried out for the . . . $4d^85s^25p$ configuration and the experimental results correspond to the . . . $4d^85p$ configuration of In.

timated. This is partly due to the neglect of the correlation effects, which are most remarkable for the $J = 0$ states.

At first sight the agreement between experiment and theory seems to be better in the case of In shown in Fig. 4. The experimental splitting should, however, be diminished by about 5%, because it corresponds to the . . . $4d^85p$ configuration instead of the . . . $4d^85s^25p$ configuration. This again leads to a disagreement of the same magnitude as obtained for Cd.

As a conclusion we can say that the theory clearly seems to overestimate the energy splitting. This causes a difficult problem for the comparison between the experimental and calculated profiles. The positions of the overlapping line components are very critical for the shape of total profile and thus rather small errors in the calculated line positions lead easily to rather large disagreement with the experimental spectrum. In the case of closed-shell spectra the problem is not so serious, because only very few lines lying far from each other appear in the spectra and a comparison between experiment and theory is possible even if the energy splittings do not agree. The problem becomes more serious in the case of the open-shell spectra due to the numerous energy levels both in the initial and final states (see Fig. 2 for final state) between which the transitions can take place.

Apart from the energy splitting, the redistribution of the intensity also influences the formation of the theoretical profile. The calculation procedure used to obtain the redistribution of the intensity is described in detail in Ref. 8. The method which used the MCP program of Grant[7] to calculate the angular parts of the electrostatic interaction matrix elements, produces the intensity distribution of any open-shell atom. In this work the radial integrals are obtained from the tables of McGuire.[9] The use of the radial integrals obtained with the relativistic continuum wave functions has been found to affect only very slightly the theoretical profiles of the $M_{4,5}N_{4,5}N_{4,5}$ spectra around Cd in our other studies, which are under work at the moment.

The calculated Auger spectra of Cd to Sn are shown in Fig. 5. The width and shape of the line used in the formation of the profiles was chosen to give the best resemblance to the experiment. A comparison with the experimental spectra of Cd, In, and Sn, depicted in Fig. 1, shows fair overall agreement between calculated and experimental profiles. However, owing to the differences in the calculated and experimental energy splittings the resemblance is not excellent, especially in the case of In. The correspondence seems to be slightly better for Sn.

The calculated and experimental absolute energies seem to agree within 2 eV. The agreement is of the same order for Cd and In and slightly better for Sn.

As the next step, we tried to reproduce the theoretical profile of In by using the final-state energy splitting calculated for . . . $4d^85s^25p6s^2$ configuration. The Slater integrals calculated for a neutral atom instead of a doubly ionized ion were usually found to agree better with experiment.[10] The above-mentioned approach, however, did not lead to a much better agreement with experiment. Further research is thus needed to obtain a better picture for the experimental energy splitting. Furthermore, a reliable comparison between calculated and experimental intensities is not possible as long as the theoretical estimates for energy splittings do not agree better with experiment.

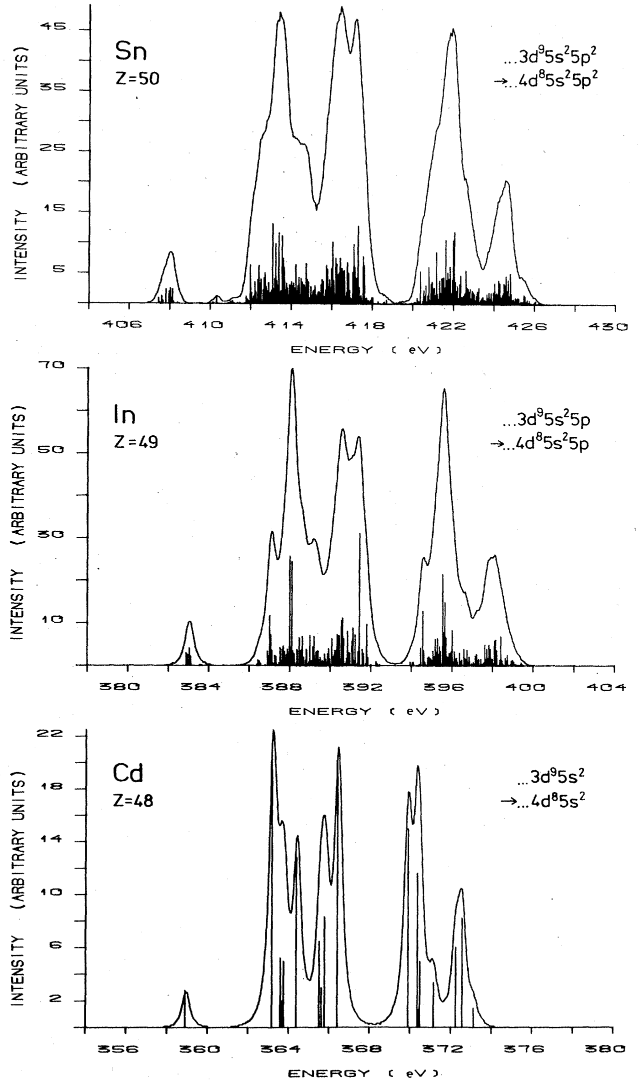

FIG. 5. Theoretical profiles of the $M_{4,5}N_{4,5}N_{4,5}$ Auger transitions of Cd, In, and Sn.

As already pointed out, a drastic change in the profiles of the studied spectra clearly appears in going from a closed-shell atom to the open-shell atoms. The theory, which completely takes into account the open-shell structure is absolutely needed to describe the experiment. Furthermore, Auger spectra of non-closed-shell atoms serve as a critical test for the fairness of the theory.

The changes in the structures of atomic spectra should also be taken into account when determining the free-atom solid kinetic-energy shifts. Thus, the experimental energy shifts of 11.8, 13.0, and 12.2 eV for Cd (Refs. 11 and 12), In (Refs. 11 and 12), and Sn, respectively, are not very accurate for In (Refs. 11 and 12) and Sn due to different fine structures of the spectra of open-shell atoms and solids. Semiempirical calculations[11,13] based on the thermochemical model agree well with the experimental values.

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[1] S. Aksela, J. Väyrynen, H. Aksela, and S. Pennanen, J. Phys. B **13**, 3745 (1980).

[2] C. E. Moore, Natl. Bur. Stand. U.S. Circ. No. 467, Vol. III (1959).

[3] Y. N. Josh, Th. A. M. Van Kleef, and V. S. Kushawaha, Can. J. Phys. **54**, 889 (1976).

[4] J. Väyrynen and S. Aksela, J. Electron Spectrosc. **16**, 423 (1979).

[5] H. Aksela, S. Aksela, and H. Patana, Phys. Rev. A **30**, 858 (1984).

[6] S. Aksela, H. Aksela, M. Vuontisjärvi, J. Väyrynen, and E. Lähteenkorva, J. Electron Spectrosc. **11**, 137 (1977).

[7] J. P. Grant, B. J. Kenzie, and P. H. Norrington, Comput. Phys. Commun. **21**, 207 (1980); *ibid.* **21**, 233 (1980).

[8] H. Aksela, T. Mäkipaaso, V. Halonen, M. Pohjola, and S. Aksela, Phys. Rev. A **30**, 1339 (1984).

[9] E. J. McGuire, Sandia Laboratories Research Report No. SC-RR 710835 (1972).

[10] H. Aksela, J. Electron Spectrosc. **19**, 371 (1980).

[11] S. Aksela, R. Kumpula, H. Aksela, and J. Väyrynen, Phys. Scr. **25**, 45 (1982).

[12] M. Pessa, A. Vuoristo, M. Valli, S. Aksela, J. Väyrynen, T. Rantala, and H. Aksela, Phys. Rev. B **20**, 3115 (1979).

[13] N. Mårtensson, P. Hedegård, and B. Johansson, Phys. Scr. **29**, 154 (1984).