Satellites in the X-Ray Emission Spectra of Li, Be, and Na†

E. T. Arakawa and M. W. Williams
Health Physics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830
(Received 10 May 1973)

The K-x-ray emission spectra for Li and Be and the L-x-ray emission spectrum for Na have been recorded. In each case a single low-energy and a single high-energy satellite were observed. The low-energy satellites are associated with the creation of volume plasmons, while the high-energy satellites result from double ionization of the relevant core levels and do not involve volume plasmons.

INTRODUCTION

The circumstances and the extent to which plasmons are involved in the production of x-ray satellites have recently become of interest. Satellites on the low-energy side of the $L_{2,3}$ bands of Na, Mg, and Al have been shown[1] to be associated with volume-plasmon creation. In filling a vacancy in the $L_{2,3}$ core levels of one of these atoms, the deexcitation energy may be shared between a photon (which is seen as a low-energy satellite) and a volume plasmon which is created in the material. It is theoretically possible[2] that the deexcitation energy may be augmented by the volume-plasmon energy, forming a satellite at an energy higher than the ordinary x-ray emission. In this case, high-energy electrons incident on the material would create both the core-electron excitation and volume plasmons. To result in high-energy-satellite emission, the atomic excitations and volume-plasmon excitations must have overlapping wave functions and comparable half-lives. We have studied[3] previously the high-energy x-ray satellites of the $L_{2,3}$ emission bands of Na, Mg, Al, and Si. Although the possibility of volume-plasmon involvement could not be ruled out completely, the results indicated that the primary contribution to the high-energy satellite for each of these elements came from the radiative decay of a double-ionization state, specifically, a double vacancy in the $L_{2,3}$ shell.

Similar events have been observed in Auger spectra. Electrons resulting from the major Auger event can either lose energy in creating a volume plasmon or gain energy from a volume plasmon on passing through the medium. In addition, electrons in a high-energy Auger satellite can originate from atoms in which the relevant core level is doubly ionized. In many cases a knowledge of the energy separation of the major Auger peak and a high-energy satellite is insufficient information to identify the mechanism involved. Jenkins *et al.*[4] examined the Auger spectrum of Be because, for this element, the energies of electrons gaining a volume-plasmon energy and those arising from double-ionization decay were calculated to be sufficiently different that it could be determined which mechanism occurs. They saw two high-energy satellites, one of which was associated with plasmon gain, while the other was associated with double ionization. We chose to study Be in light of these Auger-spectrum results. Similarly, for Li, the high-energy satellites predicted for the two effects are widely separated in energy. Interestingly, recent Auger spectra[5] for Li and Mg do not show any evidence of plasmon gain, and no low-energy x-ray satellite had been seen previously for Li. We had presented previously the data for Na in a selected spectral region; in this paper we present the spectrum for the whole range of interest.

The present studies show that for Li, Be, and Na low-energy satellites involve volume plasmon creation, whereas high-energy satellites result from double-ionization decay and do not involve volume plasmons. Thus the present studies are consistent with the previous interpretations of x-ray spectra.

EXPERIMENTAL PROCEDURE

Electrons from an electron gun were incident on samples of Li, Be, and Na. The photons emitted were dispersed by a soft-x-ray scanning monochromator and then detected in the first order using a channel electron multiplier from which the output current was read with a logarithmic electrometer. Details of this experimental apparatus have been given previously.[3]

The Li and Na samples were vacuum evaporated *in situ* and were at least 99.99% pure. The films, which could be considered infinitely thick, were deposited directly onto the water-cooled Cu anode. The pressure in the experimental chamber was $(3-5)\times10^{-7}$ torr. The Be was a bulk sample which was freshly cut and smoothed with emory cloth before insertion in the experimental chamber. Prior to taking measurements a fresh Be surface was exposed by abrading the sample, *in situ*, with a stainless steel brush.

Electrons were used with energies from 0.6–2.5 keV and beam currents from 1–10 mA. The x-ray intensities were roughly proportional to the

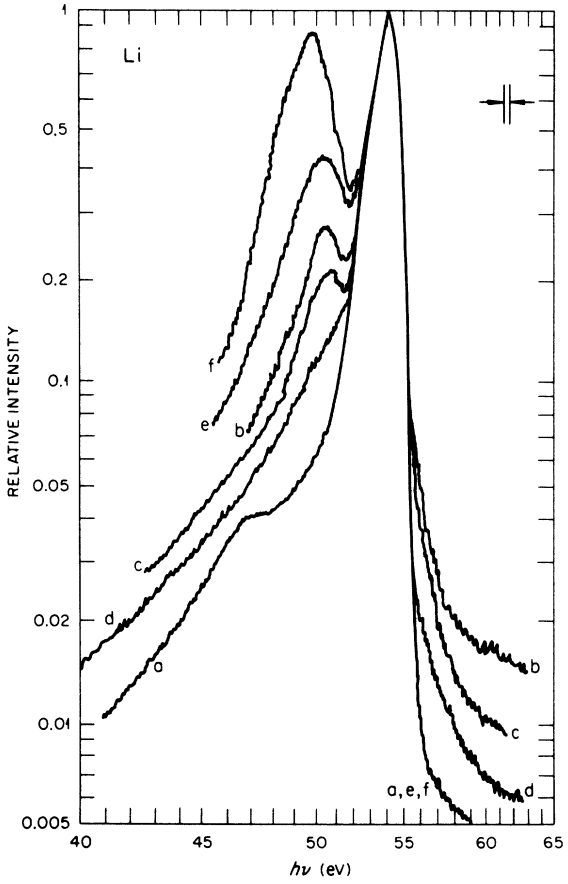

FIG. 1. Recorder traces of K-emission spectra of Li showing the dependence on electron energy and time after film deposition. (a) 2.5 keV, 2 min; (b) 0.6 keV, 30 min; (c) 1.0 keV, 35 min; (d) 1.5 keV, 40 min; (e) 2.5 keV, 55 min; (f) 2.5 keV, 90 min. The pressure was 5×10^{-7} torr. The spectral slit width in eV is shown in the figure.

electron beam current, but the structure in the x-ray spectra for the pure metals had virtually no dependence on electron energy over the experimental range of energies. The scanning speed was adjusted so that the resolution was limited only by the slit width of 200 μ. It was found that both Be and Na remained stable with time. The x-ray emission spectrum of Li showed changes, due to contamination, with time after film deposition. The "clean" surface spectra are presented for all three metals, together with spectra for Li as a function of time and electron beam energy.

RESULTS AND DISCUSSION

Shown in Fig. 1 (curve a) is the $K\alpha$ emission spectrum from clean Li metal taken within two minutes after film deposition. The main peak at 54.5 eV has been studied extensively,[6-9] but the structure in the vicinity of 47 eV has not been reported previously in the literature. The leading edge of this satellite occurs 7 eV below the leading edge of the main $K\alpha$ emission band. Thus this low-energy satellite can be associated with volume-plasmon creation since the loss of ~ 7 eV by the satellite photons agrees well with the plasmon energy of 7.12 eV reported by Kunz[10] from characteristic electron-energy-loss experiments. Curves b–f in Fig. 1 show both time and electron-beam-energy dependence of the emission spectrum. For low beam energies (0.6 and 1.0 keV, curves b and c at 30 and 35 min) the spectra show structure due to surface contamination at short times after film deposition. The low-energy electrons do not penetrate very deeply, and thus the observed emission comes from both the thin surface-contamination layer and from the Li. For a beam energy of 1.5 keV at 40 min curve d shows that the effects of contamination on the emission spectrum are less since most of the higher-energy electrons pass through the surface layer before depositing energy in the Li. Curves e and f show that eventually, even with 2.5-keV electrons, the effects of contamination are seen and that they increase with time after film deposition. Thus curves b, c, and d show, for approximately the same time, how the effects observed owing to contamination depend on the electron beam energy. The lower the electron beam energy, the earlier that contamination effects show up in the emission spectrum. Curves a, e, and f, taken with 2.5-keV electrons but at different times after film deposition, show the structure due to contamination increasing in intensity with time after film deposition. The contaminant has not been identified but is presumably due to the growth of an oxide layer on the Li surface. It is known[11] that partial oxidation of some metallic samples results in an additional peak a few electron volts below the main emission peak. It should be stressed that the plasmon satellite in the region of 47 eV is seen only for the "clean" Li spectrum obtained using high-energy electrons very soon after film deposition.

Figure 2 shows a complete K-emission spectrum obtained for Li within two minutes of film deposition. The electron energy was 2.5 keV and the electron beam current 4.8 mA. The anomalous shape of the Li K-emission spectrum is well known and has been discussed extensively.[9,12] In this respect our data are in general agreement with previously reported K-emission spectra for Li. The K-emission peak shown in Fig. 2 occurs at 54.5 eV. The low-energy satellite, ~ 7 eV below the K-emission peak, has been shown in this paper to be consistent with plasmon creation. The high-energy satellite, at 83 or 28.5 eV above the K-emission peak, agrees with the value of 28.8 eV previously found by Bedo and Tomboulian[6] but not so well with the value of 33 eV reported by Cat-

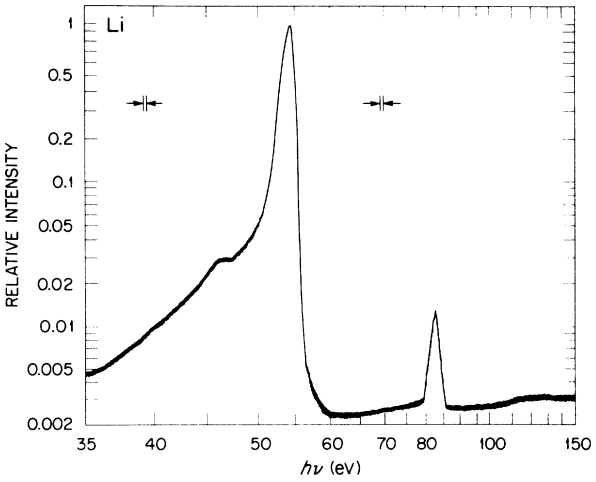

FIG. 2. Recorder trace of K-emission spectrum of Li taken less than 2 min after film deposition. The electron energy was 2.5 keV, electron beam current 4.8 mA, and the chamber pressure 3×10^{-7} torr.

terall and Trotter.[7] From the energy difference alone this satellite is not consistent with plasmon decay associated with the x-ray emission but agrees well with predictions of double-ionization theory. A two-body "hydrogen-atom-type" calculation by Nestor, of Oak Ridge National Laboratory, gives the energy difference between the main K-emission peak and the high-energy satellite as 31.78 eV, while slightly different assumptions by Hayasi[13] give 26.96 eV. In both transitions giving rise to the main and satellite emissions the lower level is a singlet, and thus one might expect the spectral shapes of the main and satellite emissions to be similar, with some broadening of the satellite band due to the shorter lifetime of the doubly ionized state. It is seen in Fig. 2 that the two bands are similar in shape, with the width at half-maximum being ~2.0 eV for the main K emission and ~2.5 eV for the high-energy satellite.

Figure 3 shows the K-emission spectrum for Be obtained with an electron energy of 2 keV and an electron beam current of 4.6 mA. The main K-emission peak is observed at 108.5 eV, a low-energy satellite at 90 eV, and a high-energy satellite at 143 eV. The K-emission band of Be has been studied previously[7,9,14–17] together with the K emission of Be in BeO.[16,17] The spectrum in Fig. 3 appears to be that for clean Be with no oxide layer, as some of the main features of the BeO spectrum observed by other workers are not seen in the present study. The shape of the main emission band is very similar to those reported previously. The only previous report of a plasmon satellite for Be was made by Watson *et al.*,[15] at an energy of 18 ± 0.5 eV below the main K emission for Be. This low-energy satellite can be associated with volume-plasmon creation since the loss of 18.5 eV by the satellite photons agrees well with the plasmon energies of 18.7[18] and 19 eV[19] derived from characteristic electron-energy-loss experiments. Figure 3 also shows a high-energy satellite 34.5 eV above the K emission of Be. This satellite has been reported at 37.6 eV[17] above the main K emission. Energy considerations eliminate the possibility of plasmon involvement in the production of this satellite, since although it falls at approximately twice the plasmon energy above the main band no high-energy satellite is seen corresponding to the single plasmon energy. The position of the satellite is consistent with double ionization and, as is expected for K-emission satellites associated with double ionization, the satellite band is similar in shape to, but slightly broader than, the main band. Calculations by Hayasi[13] assuming double ionization place the main-band–high-energy-satellite separation at 34.07 eV for Be. This energy separation was also calculated to be 39.52 eV using a computer code developed by Froese[20] involving nonrelativistic Hartree–Fock wave functions.

Jenkins *et al.*[4] observed high-energy Auger satellites 18 and 38 eV above the K Auger peak in Be. The 18-eV separation identifies this satellite as due to Auger electrons gaining 18 eV by volume-plasmon decay in the bulk Be. We do not see this peak in our x-ray spectrum. However, the probability of volume-plasmon gain by Auger elec-

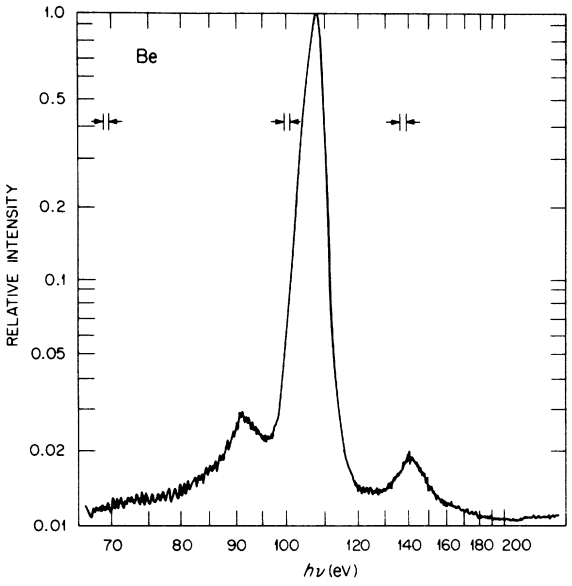

FIG. 3. Recorder trace of K-emission spectrum of Be. The electron energy was 2 keV, electron beam current 4.6 mA, and the chamber pressure 5×10^{-7} torr.

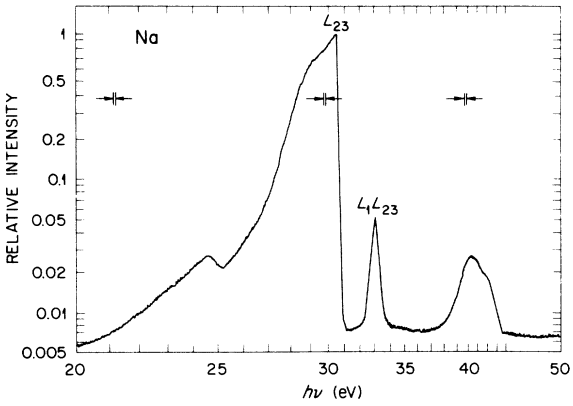

FIG. 4. Recorder trace of L-emission spectrum of Na. The electron energy was 2.5 keV, the electron beam current 3.5 mA, and the chamber pressure 5×10^{-7} torr.

trons passing through the material is much greater than the probability of creating a high-energy x-ray photon by the simultaneous decay of a core-level electron and a volume plasmon. The satellite 38 eV above the K Auger peak could be attributed to double-plasmon gain or to double ionization of the K level in Be.

Figure 4 shows the L-emission spectrum of Na obtained with an electron energy of 2.5 keV and an electron beam current of 3.5 mA. The high-energy edge of the low-energy satellite in Fig. 4 occurs ~ 5.5 eV below the high-energy edge of the main L_{23} emission, agreeing with the value of 5.5 ± 0.2 eV observed by Rooke.[12] This low-energy satellite is associated with plasmon creation since the volume-plasmon energy of Na has been determined as 5.85 eV[21] from characteristic-electron-energy-loss measurements and 5.49[22] and 5.69 eV[23] from optical measurements. We have previously reported measurements[3] on the main L_{23} emission, the L_3-L_1 emission, and the high-energy satellite. From consideration of the energy separation between the main band and the high-energy satellite and from a detailed analysis of the shape of the high-energy satellite, it was concluded that this satellite is associated with double ionization and not plasmon decay. Catterall and Trotter[7] give a similar analysis of the high-energy satellite in Na.

CONCLUSIONS

It is concluded that the low-energy satellites associated with the x-ray emission spectra of Li, Be, and Na involve plasmon creation, whereas the high-energy satellites involve double ionization, but not plasmon decay.

ACKNOWLEDGMENT

The authors wish to thank W. C. Nestor for calculating the energies of the high-energy satellites of Li and Be assuming double ionization.

†Research sponsored by the U.S. Atomic Energy Commission under contract with Union Carbide Corp.

[1]G. A. Rooke, Phys. Lett. **3**, 234 (1963).
[2]V. V. Shmidt, Zh. Eksp. Teor. Fiz. **39**, 1269 (1960) [Sov. Phys.-JETP **12**, 886 (1961)].
[3]W. F. Hanson and E. T. Arakawa, Z. Phys. **251**, 271 (1972).
[4]L. H. Jenkins, D. M. Zehner, and M. F. Chung, Surf. Sci. **38**, 327 (1973); L. H. Jenkins and D. M. Zehner, Solid State Commun. **12**, 1149 (1973).
[5]H. Löfgren and L. Walldén, Solid State Commun. **12**, 19 (1973).
[6]D. E. Bedo and D. H. Tomboulian, Phys. Rev. **109**, 35 (1958).
[7]J. A. Catterall and J. Trotter, Philos. Mag. **3**, 1424 (1958).
[8]R. S. Crisp and S. E. Williams, Philos. Mag. **5**, 525 (1960).
[9]O. Aita and T. Sagawa, J. Phys. Soc. Jap. **27**, 164 (1969).
[10]C. Kunz, Z. Phys. **196**, 311 (1966).
[11]K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, *ESCA Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy* (Almqvist and Wiksells Boktryckeri AB, Uppsala, Sweden, 1967), p. 224.
[12]G. A. Rooke, in *Soft X-Ray Band Spectra and the Electronic Structure of Metals and Materials*, edited by D. J. Fabian (Academic, New York, 1968), p. 3.
[13]Y. Hayasi, Sci. Rep. Tohoku Univ. 1 **52**, 41 (1969).
[14]G. Wiech, in Ref. 12, p. 59.
[15]L. M. Watson, R. K. Dimond, and D. J. Fabian, in Ref. 12, p. 45.
[16]A. P. Lukirskii and I. A. Brytov, Fiz. Tverd. Tela **6**, 43 (1964) [Sov. Phys.-Solid State **6**, 33 (1964)].
[17]Y. Hayasi, Sci. Rep. Tohoku Univ. 1 **51**, 1 (1968).
[18]O. Sueoka, J. Phys. Soc. Jap. **20**, 2203 (1965).
[19]C. J. Powell, Proc. Phys. Soc. Lond. **76**, 593 (1960).
[20]C. Froese, Can. J. Phys. **41**, 1895 (1963); University of British Columbia Computing Center Report, September, 1969 (unpublished).
[21]J. B. Swan, Phys. Rev. **135**, A1467 (1964).
[22]H. Mayer and B. Hietel, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abelès (North-Holland, Amsterdam, 1965), p. 47.
[23]J. C. Sutherland, E. T. Arakawa, and R. N. Hamm, J. Opt. Soc. Am. **57**, 645 (1967).