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Energy dispersion of Auger electrons in resonant excitation of the Mo $2p_{3/2}$ orbital in Mo and Li_2MoO_4

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Abstract. The Mo $L_3M_{4,5}M_{4,5}$ Auger electron spectra have been measured with tubable synchrotron radiation in the vicinity of the Mo $2p_{3/2}$ absorption edge. It has been found that the $L_3M_{4,5}M_{4,5}$ Auger lines shift to a higher kinetic energy with increasing photon energy, about 4 eV for Mo and about 12 eV for Li_2MoO_4. It is also shown that the $L_3M_{4,5}M_{4,5}$ Auger lines of Li_2MoO_4 are split into two-peak structures just above the resonant Mo $2p_{3/2} \rightarrow 4d(5s)$ excitation, which are assigned as the spectator and normal Auger transitions. The peculiarities in the Li_2MoO_4 case are interpreted in terms of the Auger resonant Raman scattering of the incident photons and band-like structures of the unoccupied molecular orbitals in the insulating solid.

1. Introduction

Excitation of the core-orbital electron to an empty resonance state results in two principal decay processes. The excited electron either can remain as a spectator or can take part in the recombination process. The former process is called a spectator resonant Auger transition or in short a spectator Auger transition and the latter a direct-recombination or a participator Auger transition. The participator Auger transition manifests itself as an enhanced intensity of the corresponding photoline, whereas the spectator Auger transition will produce a spectrum which is roughly similar to the corresponding normal Auger spectrum.

Crasemann and co-workers [1, 2] have observed, in the spectator Auger transitions in rare-gas atoms peak splittings and energy shifts of the Xe $L_3M_{4,5}M_{4,5}$ Auger lines to higher kinetic energies by 8 eV in proportion to the excitation photon energies. The observation was attributed to the Auger resonant Raman scattering, based on the analogy of the linear Raman dispersion of luminescent KL_3 (i.e. $K\alpha_1$) x-rays from copper in the Cu 1s resonant excitation [3]. As for the spectator Auger transitions in solid, similar phenomena were reported by Elango *et al* [4] for resonant photoemission phenomena of the $2p_{1/2}$ and $2p_{3/2}$ orbitals of argon-like ions such as Cl^-, K^+, Ca^{2+} and Sc^{3+} in ionic solids, and by Kivimäki *et al* [5] for resonant super-Coster–Kronig spectra of the Ge $M_{2,3}M_{4,5}M_{4,5}$ transitions in solid Ge.

Recently we have examined the resonant photoemission of the Si 1s orbital of silicon compounds [6, 7] and found that the Si $KL_{2,3}L_{2,3}$ Auger lines of elemental silicon remain at almost constant energy, while those of insulating silicon compounds such as SiO_2 and Si_3N_4 split into two peaks and shift 4–5 eV towards higher kinetic energies with increasing photon energy. This observation suggests that the resonant behaviours in solids depend on the unoccupied molecular-orbital states which may influence the resonant photoexcitation processes.

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The aim of this work is to study the spectator Auger transitions in solids and to elucidate a correlation of the peculiar phenomena with the unoccupied molecular-orbital states. For this purpose it seems very important to compare the Auger transitions in compounds having the same element but different electronic structures. Furthermore transitions including valence electrons should be avoided in order to distinguish the spectator Auger process from the participator process. Thus one is forced to employ excitations of deep core orbitals. In this paper we chose the Mo $2p_{3/2}$ orbital (about 2530 eV in binding energy) for the resonant excitation. Observations of the peak splittings and energy dispersion of the $L_3M_{4,5}M_{4,5}$ (i.e. $2p_{3/2}^{-1}3d^{-1}3d^{-1}$) Auger lines in Mo metal and insulating Li_2MoO_4 are presented.

2. Experimental details

Experiments were carried out using synchrotron radiation from beam line 27A at the Photon Factory in the National Laboratory for High Energy Physics (KEK–PF), Japan. The radiations were monochromated with a double-crystal monochromator, providing an energy resolution of better than 1.3 eV at a photon energy of 2500 eV. The electron spectra were measured with a VSW Class-100 instrument employing a hemispherical electron energy analyser fitted to an ARIES-50 spectrometer and were recorded in counts per second (cps) mode. The analyser was operated under the fixed analyser transmission mode which yielded a full width at half-maximum of 0.9 eV for a pass energy of 10 eV, and 1.2 eV for a pass energy of 44 eV, for the Au $4f_{7/2}$ line at a photon energy of 2100 eV. The energy calibration of the spectra was based on Au $4f_{7/2}$ line of Au metal (purity, 99.99%) at 84.0 eV, or on the O 1s line of Li_2MoO_4 at 532.0 eV. The work function of the measuring system was determined to be 4.3 eV.

X-ray absorption near-edge structure (XANES) spectra were recorded with a constant-final-state mode, i.e. recording both the total electron yield and the partial electron yield (PEY) by scanning the photon energy. To avoid superposition of the O 1s line (about 2000 eV in kinetic energy) and the Mo $L_3M_{2,3}M_{2,3}$ Auger lines (1900–2100 eV) the kinetic energy of the secondary electrons in the PEY measurement was adjusted to be 1700 eV for Mo and 1970 eV for Li_2MoO_4 using the electron analyser.

The metallic sample was Mo plate, (purity, 99.95%) from Fruuchi Chemicals Ltd. The Li_2MoO_4 sample was prepared by cooling at a rate of 2 °C hr^{-1} from its melt at 850 °C, using a platinum crucible. The single crystal obtained was cleaved just before introduction to the analyser chamber. Photoinduced decomposition of the Li_2MoO_4 sample was checked by recording the photoemission lineshapes of the Mo $2p_{3/2}$ and Mo 3d regions and was confirmed to be less than the detection limit. The other details have been given elsewhere [6–8].

3. Results and discussion

Figure 1 shows XANES spectra in the vicinity of the Mo $2p_{3/2}$ absorption edge. The absorption at around 2522–2540 eV is attributed to resonant excitation from the Mo $2p_{3/2}$ ground state to unoccupied orbitals which are mainly composed of the Mo 4d(5s) orbitals considering the dipole selection rule. As the Mo $2p_{3/2}$ ionization energies determined by XPS with 2845.0 eV photons are 2523.5 eV for Mo and 2527.8 eV for Li_2MoO_4, the resonance excitation begins at 2–13 eV below the threshold.

Electronic band calculations for Mo indicate that the main structure of the density of states for the unoccupied orbitals is located at 2–2.5 eV above the Fermi level [9–12].

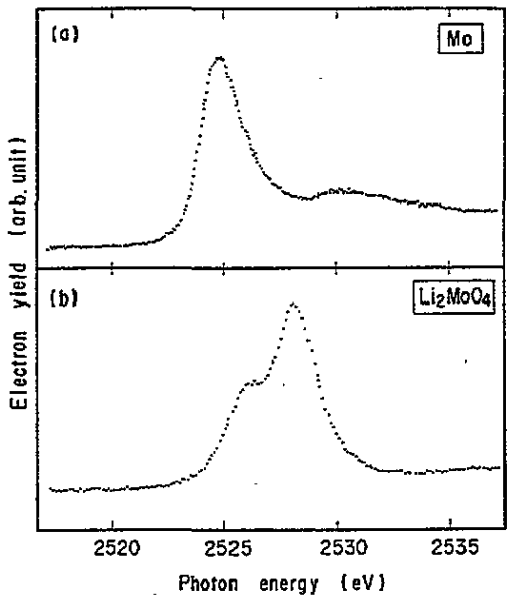

Figure 1. XANES spectra of (a) Mo metal and (b) Li_2MoO_4 at the Mo $2p_{3/2}$ absorption edge.

Furthermore the experimental isochromat spectrum of Mo gave a partial density of states ranging from 0.5 to 3.5 eV, peaking at 2.5 eV above the Fermi level [12]. Thus the spectral profile in figure 1(a) is in fair agreement with these previous studies.

Our previous calculations of molecular orbitals for Li_2MoO_4 indicate that the unoccupied orbitals with Mo 4d character are located at 5.88 eV (3e) and 8.58 eV ($9t_2$) higher than the top of the occupied orbitals [13]. Since the separation energy of the two peak components in the XANES spectrum, 2.5 eV, agrees well with the calculations, the 2525.7 eV peak and 2528.2 eV peak are assigned as the Mo $2p_{3/2} \rightarrow 3e$ and Mo $2p_{3/2} \rightarrow 9t_2$ transitions, respectively.

The photon energy dependence of the Mo $L_3M_{4,5}M_{4,5}$ Auger electron spectra of Mo is presented in figure 2. The three-peak structure A, B, and C which is clearly seen at a photon energy of 2522.3 eV, well below the Mo $2p_{3/2}$ ionization threshold (2523.5 eV), arises from the signals from the spectator Auger transitions. On the other hand, the spectrum obtained at 2581.4 eV photon energy which is far beyond the Mo $2p_{3/2}$ absorption edge is due to the $L_3M_{4,5}M_{4,5}$ normal Auger transitions. From the resemblance between this spectrum and the $L_3M_{4,5}M_{4,5}$ normal Auger spectra of the other 4d metals such as In, Sn and Sb [14, 15], and Nb [16], the main component of peak A is assigned as the final-state term of $^1G_4$.

The photon energy dependence of the Mo $L_3M_{4,5}M_{4,5}$ Auger electron spectra of Li_2MoO_4 is presented in figure 3. The three-peak structure A, B and C is assigned as the $L_3M_{4,5}M_{4,5}$ spectator Auger transitions. Double three-peak structures at a photon energy of 2526.6 eV are probably due to the two kinds of the resonant excitation: Mo $2p_{3/2} \rightarrow 3e$ and Mo $2p_{3/2} \rightarrow 9t_2$. Whereas the former transition was seen just in the vicinity of the photon energy of 2526.6 eV, the latter transition was observed in the photon energy range 2521–2535 eV. The observation suggests that the $9t_2$ level possesses a width of about 12 eV, a part of which is distributed in the continuum. The spectator Auger lines completely disappear when obtained at a 2544.8 eV photon energy which is far beyond the Mo $2p_{3/2}$ absorption edge. Thus the uppermost profile virtually represents a spectrum for the $L_3M_{4,5}M_{4,5}$ normal Auger transitions, and the main component of peak A′ is assigned as the final-state term of $^1G_4$ [14, 15]. Peak splitting between the spectator Auger transitions and normal Auger

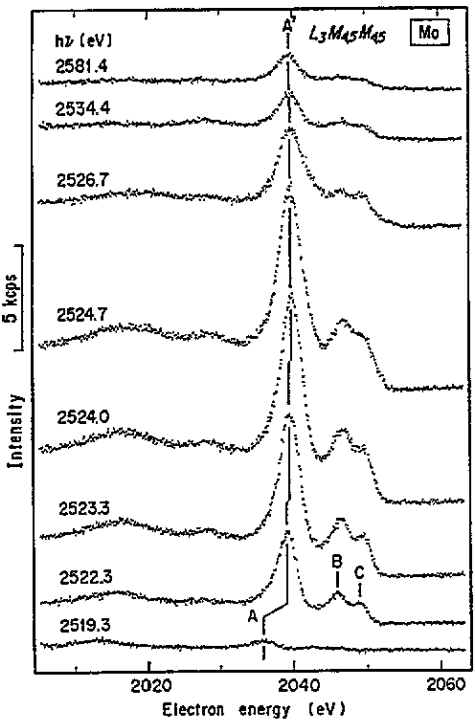

Figure 2. Mo $L_3M_{4,5}M_{4,5}$ Auger electron spectra for Mo metal taken at a pass energy of 44 eV. A′ is a line from the Mo $L_3M_{4,5}M_{4,5}(^1G_4)$ normal Auger transition.

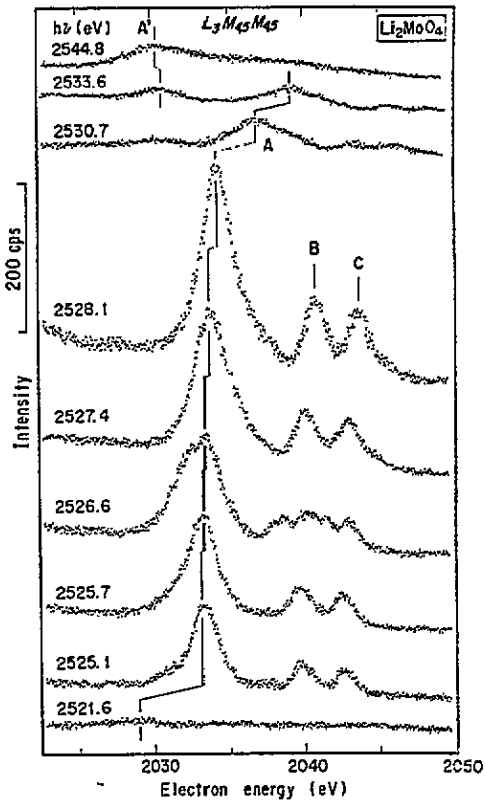

Figure 3. The same as figure 2 for Li_2MoO_4. The vertical lines in the spectra are due to the Mo $2p_{3/2} \rightarrow 9t_2$ excitation.

transitions amounts to 8.6 eV at a photon energy of 2533.6 eV.

Figure 4 shows plots of the peak energies against the photon energy determined for both the $L_3M_{4,5}M_{4,5}$ spectator Auger transition A and the $L_3M_{4,5}M_{4,5}$ normal Auger transition A′. For both samples the normal Auger line shifts slightly towards lower kinetic energies with increasing photon energy. This is due to the phenomenon well known as the post-collision interaction which causes a change in the screening of the core hole by the slowly outgoing photoelectron [17]. On the other hand, the spectator Auger line shifts towards higher kinetic energies almost in proportion to the photon energy.

Similar shifts of the spectator Auger line towards higher kinetic energies have been observed for metallic lanthanides [18, 19], semiconductors [5], ionic solids [4, 20] and rare-gas atoms [1, 2]. The photon energy dependence of the shift energy has not been given in these except in the last paper. The linear dispersion as a function of the excitation photon energy for the $L_3M_4M_5(^1G_4)$ spectator Auger transition in atomic Xe [1, 2] has been interpreted in terms of the Auger resonant Raman effect. Since such a phenomenon seems to be characteristic of the deep core hole created in the resonant excitation [3], the same energy dispersion is expected for the same transition regardless of the materials employed. Thus the diversity in the energy dispersion observed for the Mo $L_3M_{4,5}M_{4,5}$ spectator Auger transitions in the present work, about 4 eV for Mo and about 12 eV for Li_2MoO_4, requires

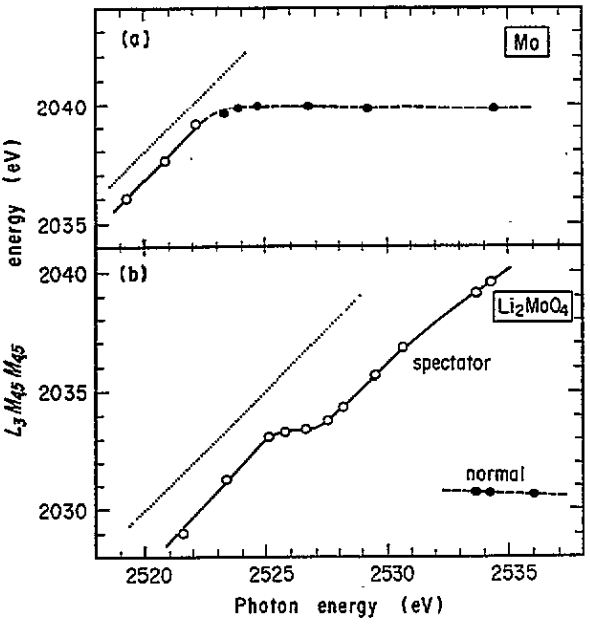

Figure 4. Mo $L_3M_{4,5}M_{4,5}$ Auger electron energy as a function of photon energy for (a) Mo metal and (b) Li_2MoO_4: ○, spectator Auger transitions; ●, normal Auger transitions, respectively: ·····, these lines indicate that a slope of 45° expected from the linear Raman dispersion.

further interpretation.

The large energy dispersion of the Mo $L_3M_{4,5}M_{4,5}$ spectator Auger lines of Li_2MoO_4 are considered to be due to the band-like structure of the unoccupied orbitals in the solid. In the present case the Mo $2p_{3/2}$ orbital electron is excited to the unoccupied molecular orbital states which may form a band-like structure having the Mo 4d atomic character. The excited electron is considered to drop to the bottom of this band immediately after the excitation and excess intra-atomic energy may be simultaneously transferred to the outgoing Auger electron from the Mo 3d orbital ($L_3M_{4,5}M_{4,5}$ Auger transition). It should be noted that the whole process of photoexcitation and Auger electron emission is almost described as a single event, because the Auger transition is so fast that it cannot be separated from the photoexcitation. Thus the transfer energy will increase with increasing photon energy until the spectator electron reaches the top of the band. This leads to the conclusion that the insulating materials whose unoccupied band is broader than that of the metals give a larger dispersion. In fact, the energy dispersion observed for Li_2MoO_4 is considered to be a sum of the contributions from the band-like structure of the unoccupied orbitals and the Auger resonant Raman process of the deep core hole.

In conclusion, we have studied the Mo $L_3M_{4,5}M_{4,5}$ Auger transitions of Mo and Li_2MoO_4 using synchrotron radiation and found that the spectator Auger line shifts to higher kinetic energies almost in proportion to increasing photon energy. The shift energies observed are about 4 eV for Mo and about 12 eV for Li_2MoO_4. The larger energy dispersion and Auger line splittings in insulating Li_2MoO_4 are interpreted in connection with the band-like structure of the unoccupied orbitals.

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References

[1] Brown G S, Chen M H, Crasemann B and Ice G E 1980 *Phys. Rev. Lett.* **45** 1937
[2] Armen G B, Åberg T, Levin J C, Crasemann B, Chen M H, Ice G E and Brown G S 1985 *Phys. Rev. Lett.* **54** 1142
[3] Eisenberger P, Platzman P M and Winick H 1976 *Phys. Rev. Lett.* **36** 623
[4] Elango M, Ausmees A, Kikas A, Nõmmiste E, Ruus R, Saar A, van Acker J F, Andersen J N, Nyholm R and Martinson I 1993 *Phys. Rev.* B **47** 11 736
[5] Kivimäki A, Aksela H, Aksela S and Sairanen O-P 1993 *Phys. Rev.* B **47** 4181
[6] Baba Y, Sasaki T A and Yamamoto H 1994 *Phys. Rev.* B **49** 709
[7] Baba Y, Yamamoto H and Sasaki T A 1994 *Surf. Sci.* **307–9** 896
[8] Konishi H, Hashimoto S, Ohno H, Sasaki T A, Yokoya A and Motohashi H *Nucl. Instrum. Methods* B at press
[9] Petroff I and Viswanathan C R 1971 *Phys. Rev.* B **4** 799
[10] Zunger A, Kerker G P and Cohen M L 1979 *Phys. Rev.* B **20** 581
[11] Jani A R, Tripathi G S, Brener N E and Callaway J 1989 *Phys. Rev.* B **40** 1593
[12] Czyzuk M T, Lawniczak-Jablonska K and Mobilio S 1992 *Phys. Rev.* B **45** 1581
[13] Sasaki T A and Kiuchi K 1981 *Chem. Phys. Lett.* **84** 356
[14] Kleiman G G, Landers R, Nascente P A P and de Castro S G C 1992 *Phys. Rev.* B **46** 1970
[15] Kleiman G G, Landers R, Nascente P A P and de Castro S G C 1992 *Phys. Rev.* B **46** 4405
[16] Landers R, Nascente P A P, de Castro S G C and Kleiman G G 1992 *J. Phys.: Condens. Matter* **4** 5881
[17] Niehaus A 1977 *J. Phys. B: At. Mol. Phys.* **10** 1845
[18] Sairanen O-P, Aksela S and Kivimäki A 1991 *J. Phys.: Condens. Matter* **3** 8707
[19] Sairanen O-P 1991 *Phys. Scr.* T **41** 163
[20] Sarma D D, Carbone C, Cimino R, Sen P, Gudat W and Eberhardt W 1993 *Phys. Rev.* B **47** 4853