

Spectator and participator Auger transitions by resonant excitation of the Mo $2p_{3/2}$ orbital in Li_2MoO_4 , MoO_3 , and MoS_2

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The Auger decay process after resonant Mo $2p_{3/2} \rightarrow 4d(5s)$ excitation in the molybdenum compounds has been studied by photoemission spectroscopy using synchrotron radiation. It was found that the Mo($L_3M_{4,5}M_{4,5}$) Auger lines are split into double-peak structures (Li_2MoO_4 and MoO_3) or broadened (MoS_2) at the resonant photon energy. These results are attributed to spectator Auger and normal Auger transitions. The spectator Auger lines were found to shift to the higher kinetic energy by 4.5–12 eV. Amount of the energy dispersions and direction of the shifts, almost in proportion to the photon energy, are interpreted in connection with bandlike structure of the unoccupied molecular orbitals in solids compared to isolated atoms or free molecules in a gas phase. The resonantly excited state was also found to decay through the direct recombination between the excited electron and core hole, leading to emission of an electron from one of the outer orbitals. This type of transition, called a participator Auger transition, was especially enhanced in the decay involving the Mo $3d_{3/2,5/2}$ orbitals with drastic change in the photoemission branching ratio of $3d_{5/2}$ to $3d_{3/2}$.

I. INTRODUCTION

It is well known that absorption of x rays is resonantly enhanced around the core-orbital ionization threshold. The excitation of the core-orbital electron to an empty resonance state can decay via two principal ways. The excited electron can either remain as a spectator, or it can take part in the recombination process. The former process is called a spectator resonant Auger transition or shortly a spectator Auger transition and the latter is a direct-recombination or a participator Auger transition. The participator Auger transition manifests itself as 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 but has slightly shifted kinetic energies.^{1–3}

The decay mode of the resonantly excited state thus generated is very important for unraveling the mechanism of photodissociation or photon-induced desorption of gaseous molecules on material surfaces, because the rates of these phenomena depend on the contribution from various decay channels. Thus the resonant Auger decay process has been analyzed extensively for rare-gas atoms⁴ and some molecules on metal surfaces.^{5–7} However, the decay process of the resonantly excited states in solids has not been fully understood except for recent investigations on transition metals^{8,9} and metallic lanthanides.^{1,10–12}

Very recently we have reported resonance photoionization phenomena of the Si $1s$ orbital of insulating silicon compounds such as SiO_2 and Si_3N_4 and observed energy shifts ~ 5 eV of the Si($KL_{2,3}L_{2,3}$) spectator Auger lines to the higher-kinetic-energy side with increasing photon

energy.^{13,14} The phenomenon observed was interpreted in connection with bandlike structure of unoccupied levels in the solids. Similar energy shifts were reported by Elango *et al.*¹⁵ for resonant photoionization phenomena of the $2p_{1/2}$ and $2p_{3/2}$ orbitals of argonlike ions such as Cl^- , K^+ , Ca^{2+} , and Sc^{3+} in ionic solids, and by Kivimäki *et al.*¹⁶ for resonant super-Coster-Kronig spectra of the Ge($M_{2,3}M_{4,5}M_{4,5}$) transitions in solid Ge.

In order to make the resonant Auger decay process in solids clearer, it seems very important to compare the decay process in compounds containing the same element but with different electronic properties. In this paper we report spectra of x-ray-absorption near-edge structure (XANES) for the Mo $2p_{3/2}$ orbital (~ 2530 eV in binding energy) in insulating Li_2MoO_4 and MoO_3 and semimetallic MoS_2 . Dominant channels in the decay process were searched for spectator Auger transitions, participator Auger transitions, and also for normal Auger transitions. It turned out that in all cases studied here the resonant photoabsorption in the Mo $2p_{3/2} \rightarrow 2p_{3/2}4d(5s)$ process gives rise to new structures in the photoemission spectra. We also demonstrate the energy distribution curves of the Mo $3d_{3/2,5/2}$ photolines around the Mo $2p_{3/2}$ threshold and anomalies of the photoemission branching ratio in the decay processes.

II. EXPERIMENT

The experiments were carried out using synchrotron radiation from beamline 27A at the Photon Factory in the National Laboratory for High Energy Physics (KEK-PF). The radiation was monochromatized by a double-crystal monochromator using the InSb(111) plane providing energy resolution better than 1.3 eV at the pho-

ton energy of 2500 eV. The electron spectra were measured with a VSW Class-100 employing a hemispherical electron energy analyzer fitted in an ARIES-50 spectrometer, and were recorded in counts per second mode. The analyzer was operated under the fixed analyzer transmission (FAT) mode with a pass energy of 44.0 eV, which yielded a full width at half maximum (FWHM) of 1.2 eV for the Au $4f_{7/2}$ line at the photon energy of 2100 eV. To minimize the effect of charging on the peak width, the surfaces of the insulating materials were flooded with low-energy electrons during the measurements. The optimum condition of the flood gun was determined to be 1.6 A and less than 0.1 V. Thus the overall energy resolution of the whole system was estimated to be better than 1.3 eV for the Mo($L_{3,4,5}M_{4,5}$) Auger electrons (~ 2030 eV). The base pressure during the measurements was less than 4×10^{-8} Pa. The polar angle of the electric vector of the incident x rays was 45° , and the takeoff angle of the incident photoelectron was surface normal.

XANES spectra were recorded with a constant-final-state (CFS) mode, i.e., recording both the total electron yield (TEY) and partial electron yield (PEY) by scanning the photon energy. To avoid superposition of the O 1s line (~ 2000 eV in kinetic energy) and the S(KLL) Auger lines (1900–2100 eV) the kinetic energy E_k of the secondary electrons in the PEY measurement was adjusted to be 1970 eV for Li_2MoO_4 , 1930 eV for MoO_3 , and 1700 eV for MoS_2 using the electron analyzer. The electron yields were normalized by the photon intensity which was monitored by a copper mesh located in front of the sample.

The Li_2MoO_4 sample was prepared by cooling at a rate of 2°C/h from its melt at 850°C using a platinum crucible. The single crystal obtained was transparent and cleaved just before the introduction to the analyzer chamber. The MoO_3 sample was prepared by oxidizing a metallic Mo disc (99.99% purity) of 10 mm $\phi \times 1$ mm at 400°C for 1 h in air, followed by slow cooling. In order to get a stoichiometric and damage-free crystalline surface the specimen was cooled at a rate of 10°C/h in an electric furnace. The thickness of the oxide overlayer was about $0.1 \mu\text{m}$, estimated from its interference color. The MoS_2 sample was a foil of molybdenite from Fruuchi Chemicals Ltd. All of the samples were heated by an electric blower just before the introduction to the preparation chamber whose base pressure was less than 4×10^{-8} Pa.

The energy calibration of the spectra was based on the Au $4f_{7/2}$ line of metallic Au (99.99% purity) at 84.0 eV, or on the O 1s line of the insulating Li_2MoO_4 and MoO_3 samples at 532.0 eV. Photoinduced decomposition of the samples was checked by recording the photoemission line shapes of the Mo $2p_{3/2}$ and Mo $3d$ regions and was confirmed to be less than the detection limit. The other details are given elsewhere.^{13,14,17}

III. RESULTS AND DISCUSSION

A. XANES spectra

Figure 1 shows XANES spectra around the Mo $2p_{3/2}$ edge as a function of the photon energy. These essential-

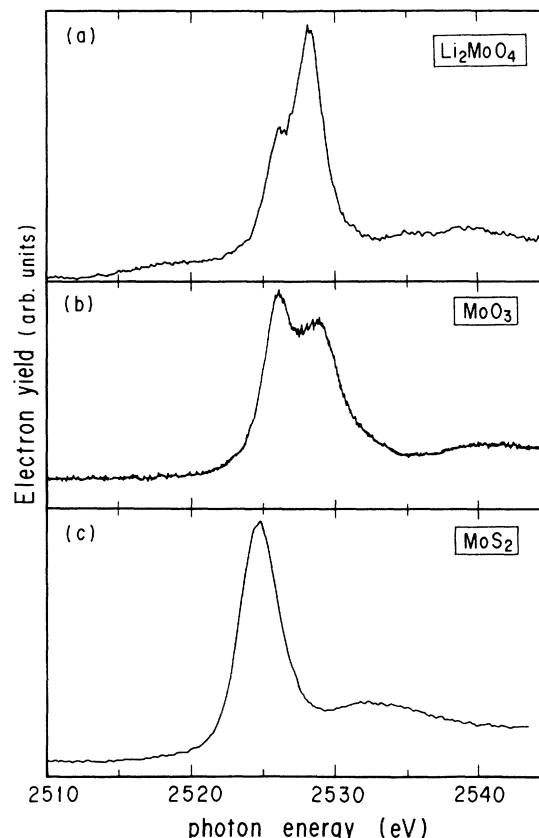


FIG. 1. XANES spectra of Li_2MoO_4 (a), MoO_3 (b), and MoS_2 (c) around the Mo $2p_{3/2}$ absorption edge.

ly represent the CFS spectra. We can see a doublet peak for the Li_2MoO_4 and MoO_3 samples, and a sharp peak for the MoS_2 sample around 2522–2540 eV. These are attributed to a 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 x-ray photoemission spectroscopy (XPS) with 2845.0-eV photons are 2527.8 eV for Li_2MoO_4 , 2527.9 eV for MoO_3 , and 2525.1 eV for MoS_2 , the resonance excitation begins at 5–13 eV below the threshold.

Our previous calculations of molecular orbitals (MO's) for Li_2MoO_4 indicated that the unoccupied orbitals with Mo $4d$ character are located at 5.88 eV ($3e$) and 8.58 eV ($9t_2$) above the top of the occupied orbitals.¹⁸ Since the separation energy of the two absorption peaks in the XANES spectrum, 2.5 eV, agrees well with the calculations, the 2525.7- and 2528.2-eV peaks are assigned to Mo $2p_{3/2} \rightarrow 3e$ and Mo $2p_{3/2} \rightarrow 9t_2$ transitions, respectively. A similar two-peak structure is also seen in the XANES spectrum of the MoO_3 sample. MO calculations for MoO_3 using the MoO_6 ideal octahedron showed a single MO of $2t_{2g}$ with the Mo $4d$ character at 3.5 eV higher than the top of the occupied orbitals.¹⁹ However, the lattice structure of this material is a fairly complex, distorted-octahedron coordination where the Mo-O distance varies over a broad range 0.188–0.245 nm.²⁰ Such distortion may result in the two-peak structure observed.

As for MoS_2 , previous MO studies have indicated that the top of the valence band is the predominantly non-bonding a'_1 orbital arising from the Mo $4d_{z^2}$ atomic orbital.^{21,22} Since the lowest unoccupied orbitals are e' and e'' orbitals with the Mo $4d$ character, the 2524.6-eV peak in the XANES spectrum is attributed to Mo $2p_{3/2} \rightarrow e', e''$ transitions. Unoccupied orbitals with the Mo $5s$ and $5p$ character are determined to be located at 7–10 eV above the a'_1 orbital by inverse photoemission spectroscopy²³ and resonant photoemission spectroscopy at the Mo $4p$ threshold.²⁴ Thus a broad weak structure centered at 2533 eV in the photon energy is assigned predominantly to the Mo $2p_{3/2} \rightarrow 5s(5p)$ transition.

B. Spectator Auger transitions by Mo $2p_{3/2}$ resonant excitations

The photon energy dependence of the Mo ($L_3M_{4,5}M_{4,5}$) Auger electron spectra of Li_2MoO_4 is presented in Fig. 2. For comparison the spectral intensities were normalized relative to the O 1s line whose intensity and peak position (referred to 532.0 eV in binding en-

ergy) should not vary in this photon energy region. A three-peak structure, A , B , and C clearly seen at 2525.1-eV photon energy, which is well below the Mo $2p_{3/2}$ ionization threshold (2527.8 eV), is the signal from the spectator Auger transitions. From the resemblance between these spectra and the $L_3M_{4,5}M_{4,5}$ Auger spectra of the other $4d$ metals such as In, Sn, and Sb,²⁵ the main components of the peaks A , B , and C are assigned to final-state terms 1G_4 , $^3F_3 + ^3F_2$, and 3F_4 , respectively. Whereas their structures become considerably broadened, their intensities are resonantly enhanced around the photon energy of ~ 2528 eV. This resonant behavior corresponds to the spectral shape of Fig. 1(a) and its threshold around 2521-eV photon energy is consistent with the rising point of the XANES spectrum. On the other hand, the spectator Auger structures have completely disappeared from a spectrum taken at 2544.8-eV photon energy which is far beyond the Mo $2p_{3/2}$ absorption edge. Thus the shape shown uppermost in Fig. 2 virtually represents a spectrum for the $L_3M_{4,5}M_{4,5}$ normal Auger transitions and the main component of the peak A' is assigned to the final-state term 1G_4 .²⁵ Peak splitting between the spectator Auger transitions and normal Auger transitions amounts to ~ 8.8 eV at the photon energy of 2533.6 eV.

Similar peak splittings or peak broadenings around the resonant photon energy were observed in the $L_3M_{4,5}M_{4,5}$ Auger electron spectra of MoO_3 and MoS_2 , shown in Figs. 3 and 4, respectively. In the case of the spectral

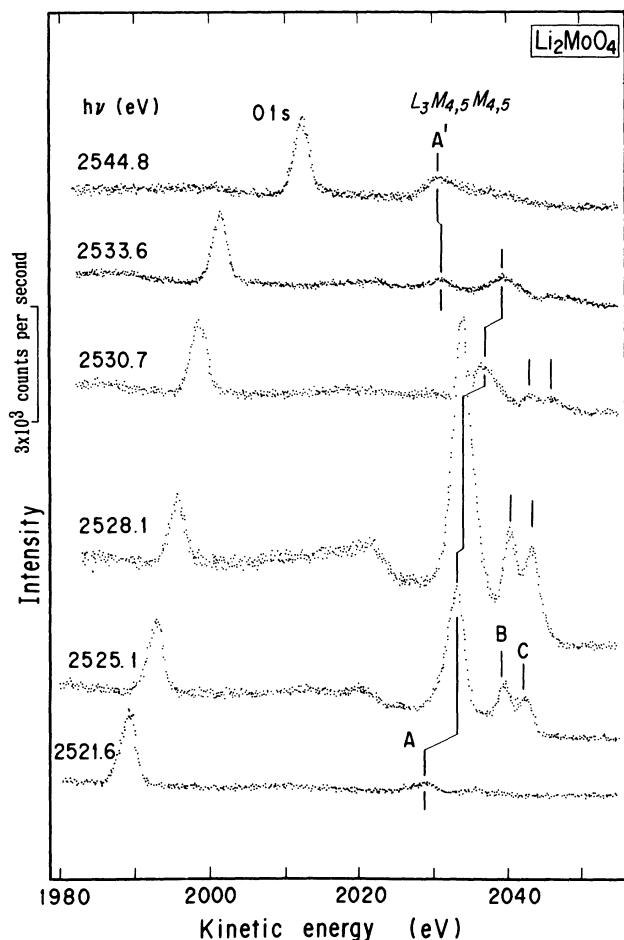


FIG. 2. Resonant Mo($L_3M_{4,5}M_{4,5}$) Auger electron spectra for Li_2MoO_4 . Main components of the peaks A , B , and C are assigned to final-state terms 1G_4 , $^3F_3 + ^3F_2$, and 3F_4 , respectively. A' stands for a line from the Mo($L_3M_{4,5}M_{4,5}$) normal Auger transition.

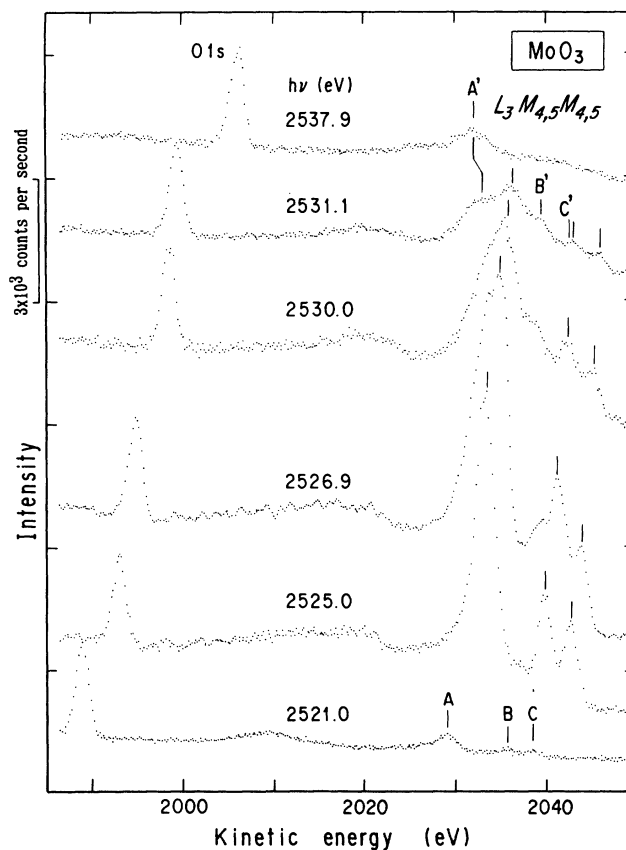
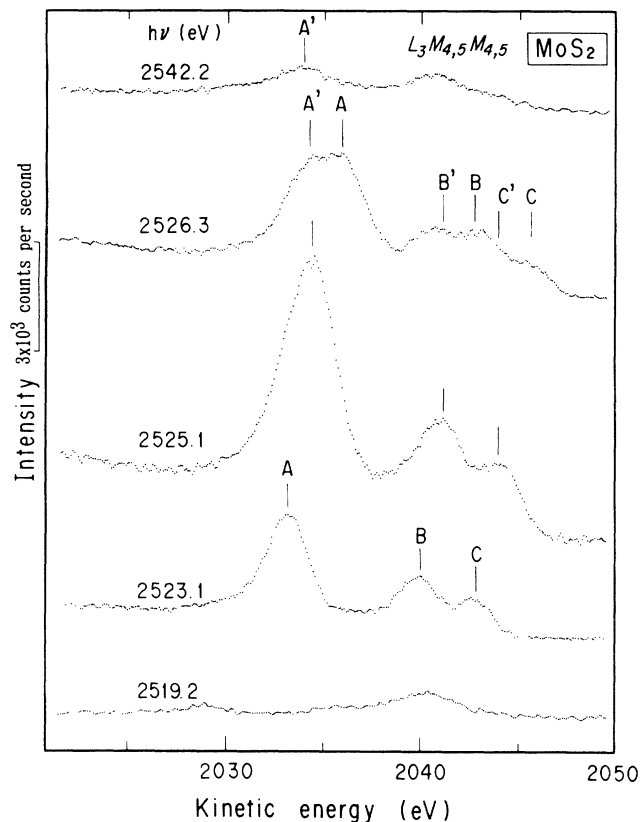


FIG. 3. Same as Fig. 2 for MoO_3 .

FIG. 4. Same as Fig. 2 for MoS_2 .

evolution of the MoO_3 sample, peak structures corresponding to both the spectator and normal Auger transitions are also clearly seen.

Precise peak positions and peak intensities were determined from deconvolution of the double three-peak structures using curve-fitting techniques. To eliminate the inconvenience of the asymmetry in the Auger lines when comparing the intensities of different lines, the background was subtracted from the spectra by the Shirley background method.²⁶ Initially, the fitting procedure was applied only to the three-peak structure of the spectator Auger transitions. The peak position, FWHM value, peak intensity, and mixing ratio between Gaussian and Lorentzian line shapes were allowed to vary. The peak separation, FWHM ratio, peak intensity ratio, and mixing ratio thus determined were then used for the fitting of the three-peak structure of the normal Auger transitions. In Fig. 5 a typical result of the curve fitting is shown for a spectrum (2530-eV photon energy) of the MoO_3 sample.

Figure 6 shows plots of the peak energies against the photon energy determined for both the $L_3M_{4,5}M_{4,5}(^1G_4)$ spectator Auger transition (A) and the $L_3M_{4,5}M_{4,5}(^1G_4)$ normal Auger transition (A'). For all of the samples the normal Auger line slightly shifts toward lower kinetic energy with increasing photon energy. This is due to the phenomenon well known as postcollision interaction.²⁷ On the other hand, the spectator Auger line shifts towards higher kinetic energy almost in proportion to the

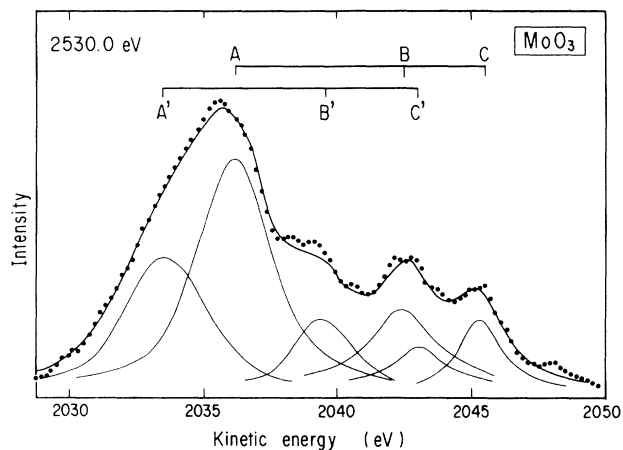


FIG. 5. Curve-fitting results for deconvolution of $\text{Mo}(L_3M_{4,5}M_{4,5})$ Auger spectrum taken for MoO_3 by 2530.0-eV photons. Curves A , B , and C are peaks for the spectator Auger transitions and curves A' , B' , and C' for the normal Auger transitions. The sums of these peaks are overlaid on the experimental spectrum.

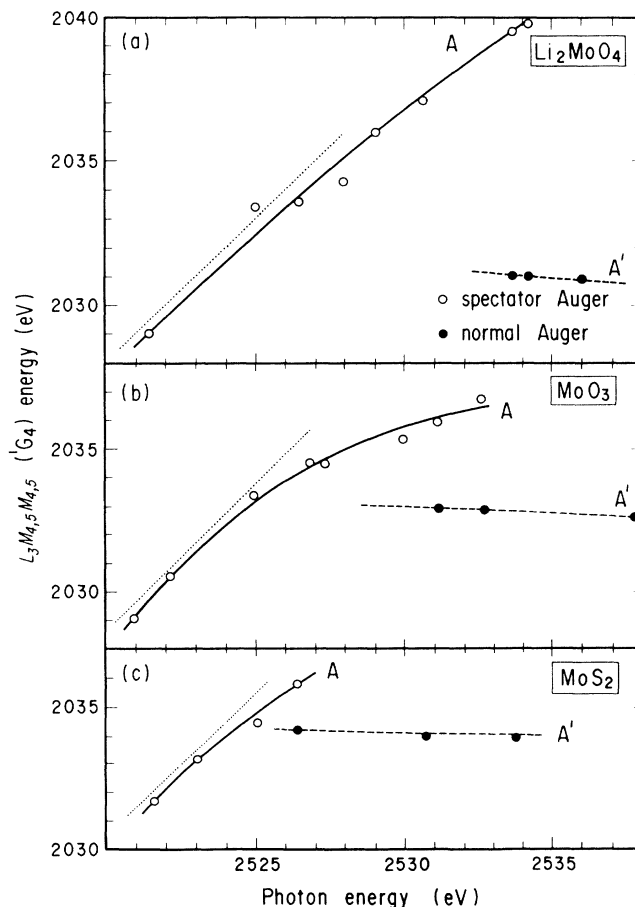


FIG. 6. $\text{Mo}(L_3M_{4,5}M_{4,5}(^1G_4))$ energy as a function of photon energy for Li_2MoO_4 (a), MoO_3 (b), and MoS_2 (c). Open and closed circles are for the spectator and normal Auger transitions, respectively. Dotted lines indicate a slope of 45° expected from the linear Raman dispersion.

photon energy.

Similar shifts of the spectator Auger line toward higher kinetic energy have been observed for condensed phases such as metallic lanthanides,^{1,10} semiconductors,¹⁶ ionic solids,¹⁵ and rare gases,⁴ and some molecules⁵⁻⁷ adsorbed on metal surfaces. Although the photon energy dependence of the shift energy has not been given in those works, its maximum value seems to be at most 4.5 eV.¹⁵ On the other hand, the linear dispersion as a function of the excitation photon energy, ~ 9 eV for the $5d$ spectator, has been found for the $L_3M_4M_5(^1G_4)$ spectator Auger transition in atomic Xe.^{28,29} This last phenomenon was interpreted in terms of the Auger resonant Raman effect. Since the effect is characteristic of the deep core hole created in the resonant excitation,³⁰ 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, ~ 12 eV for Li_2MoO_4 , ~ 8 eV for MoO_3 , and ~ 4.5 eV for MoS_2 , requires a further interpretation.

The energy dispersions in the Mo($L_3M_{4,5}M_{4,5}$) spectator Auger transitions are considered to be due to the bandlike structure of the unoccupied orbitals in solids. In the present case, the Mo $2p_{3/2}$ orbital electron would be excited to the unoccupied orbital which forms a bandlike structure having Mo $4d$ atomic character. The excited electron, or spectator, 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 (LMM transition). It should be noted that the whole process of photoexcitation and Auger transition is practically described as a single event, because the Auger process is so fast that it cannot be separated from the photon absorption. Then the transfer energy will increase with the photon energy until the spectator reaches the top of the band. This leads to the conclusion that insulating materials, whose unoccupied band is broader than that of the metals, give a large dispersion. This assumption is consistent with our observations. In fact, the energy dispersions observed are considered to be the sum of the contributions from the bandlike structure of the unoccupied orbitals and the Auger resonant Raman process of the deep core hole.

C. Participator Auger transition by Mo $2p_{3/2}$ resonant excitations

Since the photoionization cross section drastically decreases with the photon energy,³¹ we focus our attention here on only intense photolines, i.e., photoemission from the Mo $3p$ and Mo $3d$ orbitals. Moreover, spectral analyses were carried out only for the Li_2MoO_4 and MoO_3 samples, because the photolines of the Mo $3d$ and S $2s$ orbitals in the MoS_2 sample overlap each other.

Figure 7 shows a set of photoemission spectra of the Mo $3d$ region for the Li_2MoO_4 sample with various photon energies around the Mo $2p_{3/2}$ threshold. The intensities of the spectra are normalized relative to the O $1s$ line, as in Figs. 2–4. The abscissa gives the binding energy

relative to the center of the Mo $3d_{5/2}$ line as 20.0 eV. In a spectrum taken at 2511.8-eV photon energy, which is far below the threshold, the Mo $3d_{3/2}$ and Mo $3d_{5/2}$ photolines are seen with a spin-orbit splitting of 3.3 eV. When the photon energy approaches the threshold, their intensities are appreciably decreased, as seen in a spectrum taken at 2525.1-eV photon energy. Structures appearing on the lower-energy side of these photolines are assigned to the Mo (L_3M_4V) and Mo (L_3M_5V) spectator Auger lines. Further increase in the excitation photon energy gives a drastic increase in both the Mo $3d_{3/2}$ and Mo $3d_{5/2}$ line intensities. It is also noteworthy that the photoemission branching ratio of the Mo $3d_{5/2}$ to Mo $3d_{3/2}$ lines drastically decreased, as shown in a spectrum for 2528.1-eV photons. At the photon energy of 2550 eV, which is far beyond the resonant excitation, the spectral pattern is almost the same as that for 2511.8 eV photons.

Figure 8 shows a set of photoemission spectra of the Mo $3d$ region for the MoO_3 sample with various photon energies around the Mo $2p_{3/2}$ threshold. A structure appearing on the lower-energy side of the Mo $3d_{3/2,5/2}$ lines

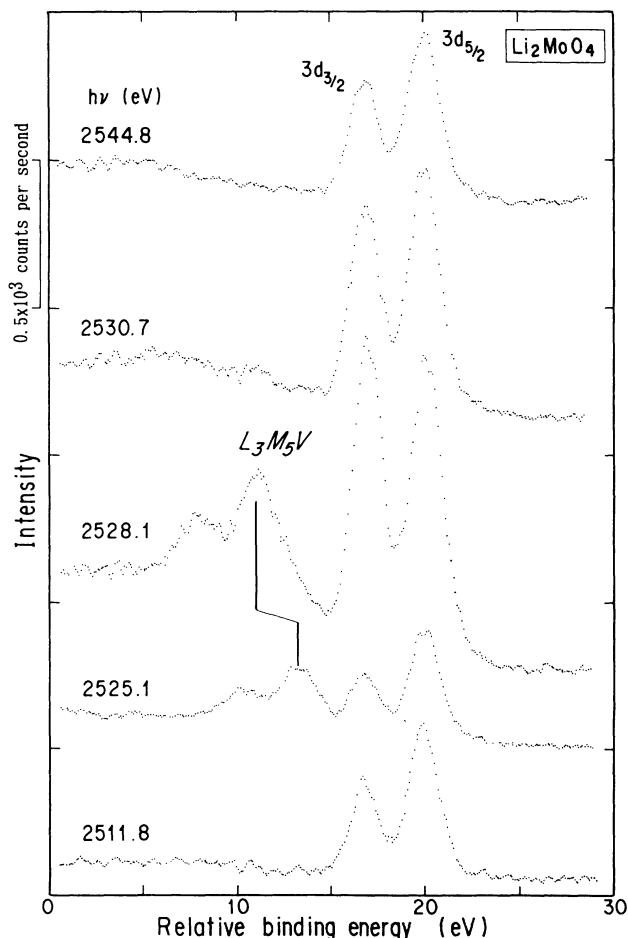


FIG. 7. Mo $3d$ photoemission spectra for Li_2MoO_4 excited with photon energies around the Mo $2p_{3/2}$ ionization threshold. Binding energies are referred to the center of the Mo $3d_{5/2}$ line as 20 eV. L_3M_5V indicates a peak from the spectator Auger transitions of the Mo(L_3M_5V) process.

is assigned to the Mo ($L_3M_{4,5}V$) spectator Auger line where the peak separation between the L_3M_4V and the L_3M_5V line is not so good as in the case of the Li_2MoO_4 sample.

The enhancements in the Mo $3d_{3/2,5/2}$ line intensities for the Li_2MoO_4 and MoO_3 samples are summarized in Fig. 9. For comparison, the photon energy dependences of the Mo $3p_{3/2}$ line intensity and sum of the Mo ($L_3M_{4,5}M_{4,5}(^1G_4)$) normal and Mo ($L_3M_{4,5}M_{4,5}(^1G_4)$) spectator Auger line intensities are also given. Since the data points plotted in this figure are by peak-area analysis, they are essentially constant-initial-state (CIS) spectra for the photolines and CFS spectra for the Auger lines. It is clearly seen that all photoline intensities decrease monotonically to the Mo $2p_{3/2}$ threshold and rise abruptly around the threshold. The overall features found are in close analogy to those observed for the $3d$ resonant photoionization cross sections of the $3d$ transition metals in atomic states and of their compounds.^{32,33}

The resonant behaviors of the photoline intensities can be interpreted in terms of the interference between direct photoemission and the nonradiative decay of the Mo $2p_{3/2}$ core hole. In the latter, the hole recombines directly with an excited electron, resulting in the emission of an electron from one of the outer orbitals (participator Auger transitions). Since the energy of the outgoing electron through the direct-recombination process is the

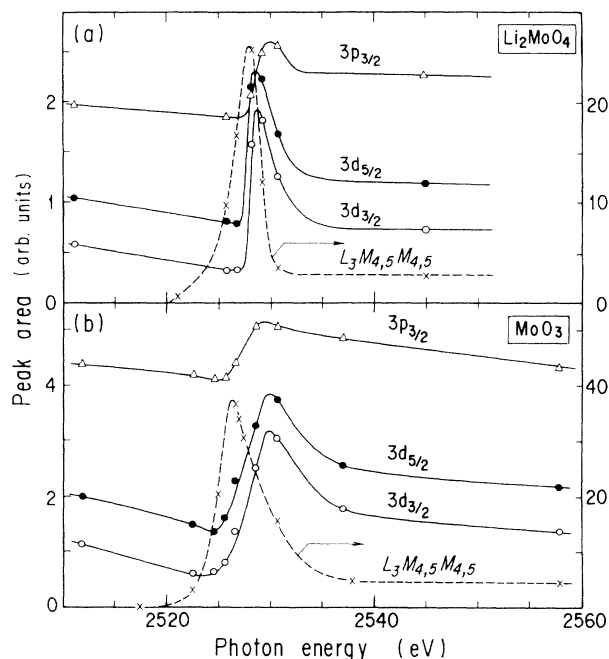


FIG. 9. Photoemission intensities of the Mo $3p_{3/2}$, Mo $3d_{3/2}$, and Mo $3d_{5/2}$ lines as a function of photon energy for Li_2MoO_4 (a) and MoO_3 (b). The dashed line is the summation of the intensities for both the spectator and normal Mo($L_3M_{4,5}M_{4,5}(^1G_4)$) Auger transitions.

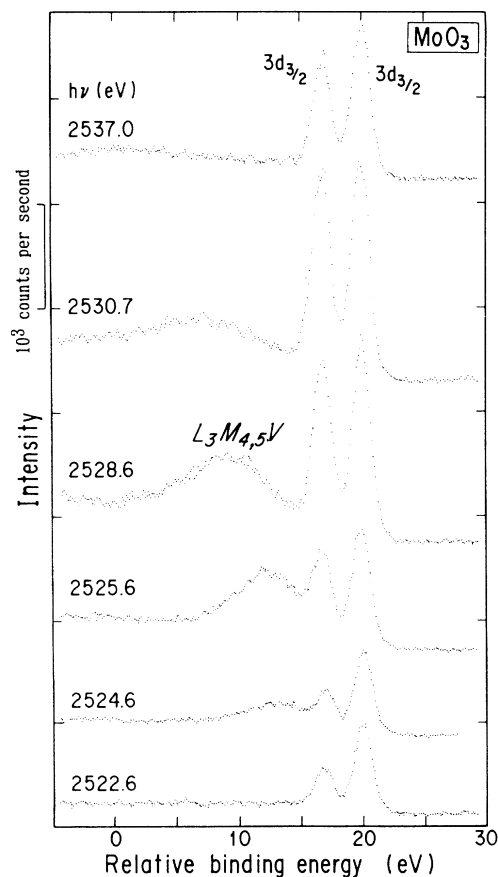


FIG. 8. Same as Fig. 7 for MoO_3 .

same as those in direct photoemission, the intensities of the corresponding $3p$ and $3d$ lines are resonantly enhanced. Asymmetric profiles are expected from theoretical treatments by Davis³² on Fano-type resonance, which exhibits a small minimum at photon energies slightly lower than the absorption-edge energy.

The enhancements in the CIS spectra for the core orbitals are observed at higher energy (1–2.5 eV for the Li_2MoO_4 sample and 3–4 eV for the MoO_3 sample) than those in the $L_3M_{4,5}M_{4,5}(^1G_4)$ CFS spectra. This implies that the higher excited states in the resonant region lead predominantly to participator Auger transitions, while the lower excited states lead to spectator Auger transitions. This trend in the decay processes agrees with that observed in the La $4d \rightarrow 4f$ resonant excitation of metallic La,¹⁰ where the $4d^9 4f^1(^3D_1)$ state excited by 101.7-eV photons decays almost entirely through $N_{4,5}O_{2,3}O_{2,3}$ and $N_{4,5}O_{2,3}V$ spectator Auger transitions, while the $4d^9 4f^1(^1P_1)$ (i.e., the giant resonance) state excited by 105–120-eV photons decays predominantly through participator Auger transitions. It should be also noted that the energy positions of the enhancement in the Mo $3p_{3/2}$ CIS spectra almost coincide with those in the Mo $3d_{3/2,5/2}$ CIS spectra. However, the degree of enhancement of the former is roughly one-half that of the latter. This means that the decay through the Mo $3d$ component is much stronger than through the Mo $3p$ component in the participator Auger transitions involving the Mo $2p_{3/2}$ core hole.

The changes in the photoemission branching ratio are more visible in Fig. 10, where the photon energy depen-

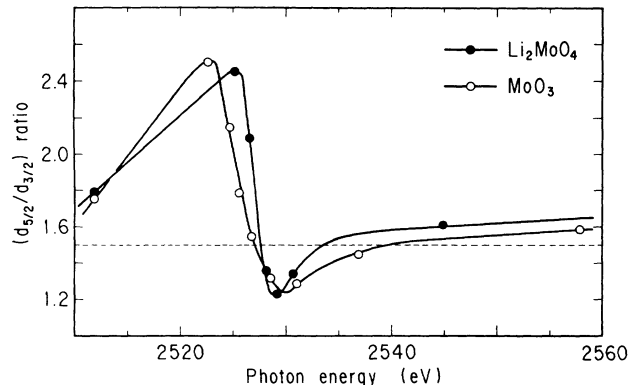


FIG. 10. Photoemission branching ratios of Mo $3d_{5/2}$ to Mo $3d_{3/2}$ lines as a function of photon energy for Li_2MoO_4 and MoO_3 . The horizontal dashed line represents the branching ratio expected from statistical degeneracy.

dences of the photoline ratio of the Mo $3d_{5/2}$ to Mo $3d_{3/2}$ orbitals are given for the Li_2MoO_4 and MoO_3 samples. Below the Mo $2p_{3/2}$ threshold the photoelectrons in the high-spin state can be emitted more easily than those in the low-spin state, while above the threshold the tendency is reversed. The ratio of the high-spin state to the low-spin state sharply drops from 2.45 at a photon energy of ~ 2524 eV to 1.25 at a photon energy of ~ 2530 eV, which deviates greatly from the statistical degeneracy of $\frac{3}{2}$ for the spin states.

Anomalies of the photoemission branching ratio have been observed for some solid samples. Sairanen¹⁰ has suggested in Tb $4d \rightarrow 4f$ resonant excitations of metallic Tb that the photoemission transition through the $5p_{1/2}$ component is much stronger than that through the $5p_{3/2}$ component. Ichikawa and his co-workers³⁴ have found anomalies of the Ba $5p_{3/2}$ to Ba $5p_{1/2}$ branching ratio in BaF_2 and the La $5p_{3/2}$ to La $5p_{1/2}$ branching ratio in LaF_3 which drop to 0.93 and 0.27 respectively, for the resonantly excited 3D_1 state. These values deviate considerably from the value of 2 expected from the statistical degeneracy of $p_{3/2}$ and $p_{1/2}$. They have interpreted their results in terms of differences in coupling between the outgoing wave of the $5p$ photoelectrons and the core holes in the final state. The fluctuations of the branching

ratio in the present work are considered to be caused by similar effects. However, detailed theoretical treatments are desired for further quantitative discussions.

IV. CONCLUSIONS

The Auger decay processes after the resonant excitation of a deep core level, Mo $2p_{3/2}$, in Li_2MoO_4 , MoO_3 , and MoS_2 samples are studied using photoemission spectroscopy with synchrotron radiation. Different resonance energies in the CIS spectra for the core-line photoemissions and CFS spectra for the Auger processes suggest that higher excited states in the resonant region lead predominantly to the participator Auger transitions and lower excited states to the spectator Auger transitions. In the decay through the Mo ($L_3M_{4,5}M_{4,5}$) spectator Auger transitions, the Auger lines shift to higher kinetic energies almost in proportion to the increasing photon energy. The shift energies observed are ~ 12 eV for Li_2MoO_4 , ~ 8 eV for MoO_3 , and ~ 4.5 eV for MoS_2 . The larger dispersion energies in the insulators are interpreted in connection with the bandlike structure of the unoccupied orbitals in the solids. In the decay through the Mo ($L_3M_{4,5}M_{4,5}$) participator Auger transitions, fluctuations of the photoemission intensities are observed for the Mo $3p_{3/2}$ and Mo $3d_{3/2,5/2}$ orbitals. The photoline enhancements at the Mo $2p_{3/2}$ absorption energy are attributed to interference between direct photoemission and nonradiative decay of the Mo $2p_{3/2}$ core hole. In the latter, the hole recombines directly with the participator, resulting in the emission of an electron from one of the outer orbitals. It is also found that the photoemission branching ratio of the Mo $3d_{5/2}$ to Mo $3d_{3/2}$ orbitals changes drastically around the Mo $2p_{3/2}$ threshold. For a full understanding of this phenomenon detailed theoretical analyses are required.

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