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Sulfur $K\beta$ x-ray emission spectra and electronic structures of some metal sulfides

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The $K\beta$ emission spectra of sulfur in α-MnS, FeS, CoS, NiS, and CuS, and in two modifications (zinc-blende and wurtzite structures) of ZnS and CdS are obtained with a two-crystal spectrometer. The spectra of FeS, CoS, and NiS consist of a broad band and are alike. The spectra from the modifications of ZnS and CdS are similar to each other. The spectrum of CuS consists of two prominent peaks and it is discussed in relation to the sulfur $K\beta$ emission spectra from α-sulfur and NiS. The $K\beta$ emission bands of ZnS and CdS are comparatively narrow, while those of the other metal sulfides are very wide. Results are evaluated by comparing the $K\beta$ emission spectra of these metal sulfides with the sulfur-K absorption spectra and with the energy-band structures.

I. INTRODUCTION

The transition-metal monosulfides (α-MnS, FeS, CoS, NiS, and CuS), ZnS, and CdS are of considerable interest in solid-state physics because of diverse electrical, optical, and magnetic effects connected with their energy-band structures. A great deal of experimental and theoretical effort[1] has been devoted to the study of the energy-band structures and related properties of ZnS and CdS, while few studies[2] for the transition-metal sulfides have been made. Recently, the energy bands of α-MnS have been calculated by Wilson[3] and the energy-band calculations for NiS have been made by Tyler and Fry[4] and by Kasowski.[5] The energy-band structures of ZnS and CdS have been calculated by many authors[6-11] using the various methods. However, energy-band calculations for FeS, CoS, and CuS have not yet been reported.

As is well known, x-ray spectroscopy provides precise and reliable information about the general electronic structure of atoms. This method is likewise powerful in elucidating certain features of the general electronic structure of solids. The x-ray valence-band emission and absorption spectra give information about the density of states in the valence and conduction bands, respectively. For example, the sulfur $K\beta$ emission and K absorption spectra of the metal sulfides reflect the distributions of the p-like states in the valence and conduction bands, respectively, and the sulfur $L_{2,3}$ emission and $L_{2,3}$ absorption spectra reflect the distributions of the s and d like states. Recently, Szargan and Meisel,[12] Sugiura *et al.*,[13] and Wiech and Zöpf[14] have measured the sulfur K and $L_{2,3}$ spectra of ZnS and CdS and explained these spectra in terms of the energy-band structures.

The sulfur $K\beta$-emission spectra of the transition-metal monosulfides have been measured by several investigators[15-18] using photographic registration. The authors[19] have found the modification effect on the sulfur $K\beta$-emission and K-absorption spectra of three crystal forms of MnS. ZnS and CdS also exist in two modifications which correspond to the zinc-blende (cubic) and wurtzite (hexagonal) structures. The modification effect on the sulfur K-absorption spectra has been investigated by Fujino *et al.*,[20] but the effect on the sulfur $K\beta$-emission spectra has not yet been reported.

The purpose of the present study is to show the sulfur $K\beta$-emission spectra of α-MnS, FeS, CoS, NiS, and CuS, and of two modifications for ZnS and CdS and to discuss the emission spectra in the light of the calculated energy-band structures.

II. EXPERIMENTAL

The sulfur $K\beta$-emission spectra were obtained by the fluorescent excitation method and recorded with a vacuum two-crystal spectrometer[21] with Ge (111) crystals. The load of the primary x-ray tube with a chromium target was about 35 kV and 35 mA. The fluorescent x-ray emitter for each sulfide was in the form of pressed polycrystalline slab. All measurements were made at (20 ± 1)°C. The detector was a flow-proportional counter using argon-methane flow gas. Pulses from the counter were stored in a multichannel analyzer. For the 2θ region ($\approx 1.5°$) investigated, 144 channels were used. The 2θ angle was scanned repeatedly at a rate of $\frac{1}{32}$°/min and the counting time for each channel was 80–140 sec. The output of the multichannel analyzer was numerically smoothed ten times with the five-point cubic least-square method.[22] After smoothing, the data were normalized with respect to the $K\beta_1$ maximum and a line was

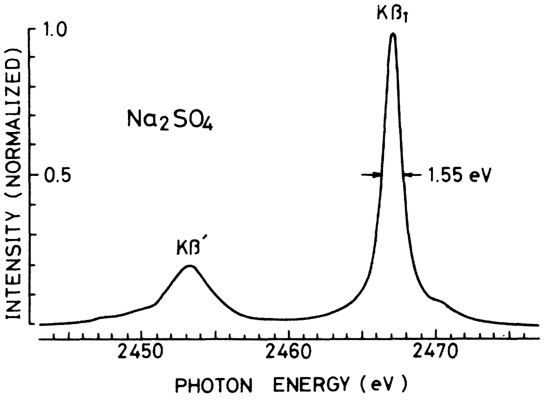

FIG. 1. Sulfur $K\beta$ emission spectrum of Na_2SO_4.

drawn to fit every point by an electronic plotter.

The transition-metal sulfides (MnS, FeS, CoS, NiS, and CuS) used here were obtained from Yamanaka Chemical Co. Two modifications of ZnS and CdS were prepared by Tanabe and coworkers. The crystal structures of these metal sulfides were identified by the x-ray diffraction method; MnS is of NaCl structure, FeS, CoS, and NiS are of NiAs structure, CuS is hexagonal, ZnS and CdS are cubic or hexagonal.

The sulfur $K\beta_1$ line (2467.15 eV) of Na_2SO_4 was used as the reference line to determine the photon energy values of the $K\beta$-emission spectra of sulfur in the metal sulfides. The sulfur $K\beta_1$ line of Na_2SO_4 is shown in Fig. 1.

III. RESULTS AND DISCUSSION

The $K\beta$-emission spectra of sulfur in α-MnS, FeS, CoS, NiS, CuS, and two modifications of ZnS and CdS are shown in Figs. 2, 3, 5, and 7. The photon energy values of the characteristic points in these spectra and the widths at half-maximum intensity ($W_{1/2}$) for the $K\beta$-emission band are given in Table I. The prominent peak β_1 occurs at nearly the same photon energy. The band widths of ZnS and CdS are much narrower than those of the other metal sulfides. The emission spectra of FeS, CoS, and NiS consist of a broad band and are similar to one another. The emission spectra of ZnS and CdS consist of a prominent peak β_1 and its subbands β_1' and β_1'', and they are alike. The spectrum of CuS is characterized by two prominent peaks β_1 and βx, and is quite different from the other spectra. The sulfur $K\beta$-emission spectra obtained here are similar to those reported previously.[12-18]

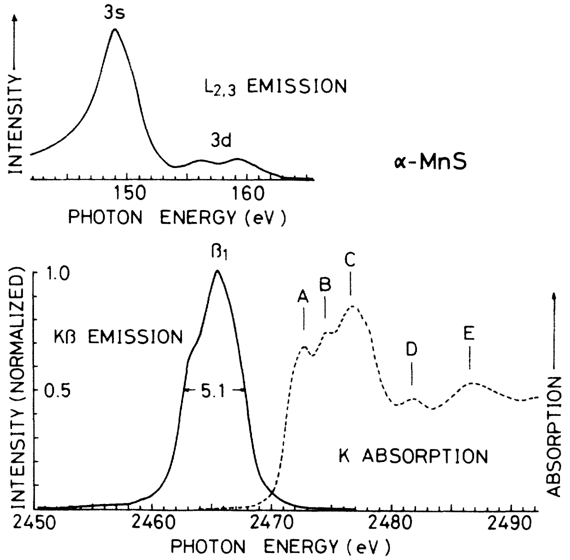

FIG. 2. Comparison of $K\beta$-emission, K-absorption (Ref. 24), and $L_{2,3}$-emission (Ref. 23) spectra of sulfur in α-MnS. The K spectra and the $L_{2,3}$-emission spectrum are joined by the photon energy (2307.77 eV) (Ref. 25) of the sulfur $K\alpha_1$ line of α-MnS.

A. α-MnS

A comparison of the sulfur $K\beta$-emission, $L_{2,3}$-emission,[23] and K-absorption[24] spectra of α-MnS is shown in Fig. 2, where the K spectra and the $L_{2,3}$-emission spectrum are joined by the photon energy (2307.77 eV)[25] of the sulfur $K\alpha_1$ line of α-MnS. The $K\beta$-emission band is much narrower than the $L_{2,3}$-emission band (which consists of two

TABLE I. Photon energy values, in eV, of the characteristic points in the $K\beta$-emission spectra of sulfur in α-MnS, FeS, CoS, NiS, CuS, and two modifications of ZnS and CdS, and the widths at half-maximum intensity ($W_{1/2}$).

	α-MnS	FeS	CoS	NiS	CuS	ZnS (cub.)	ZnS (hex.)	CdS (cub.)	CdS (hex.)
β_1''	...	...	...	...	...	2459.2	2459.0	2458.1	2457.9
β_1'	...	...	...	...	...	2463.1	2463.1	2463.8	2463.6
β_1	2465.5	2465.3	2465.3	2464.9	2463.8	2466.0	2465.8	2465.8	2466.0
βx	...	...	...	...	2467.9	...	...	...	...
half-width	5.1	5.3	4.8	5.5	6.2	3.1	3.2	2.9	2.8

characteristic parts). The main part of the $K\beta$ band appears on the high-energy side (originating from $3d$ electrons of the Mn^{2+} ion) of the main part (arising from $3s$ electrons of the S^{2-} ion) of the $L_{2,3}$-emission band. The main part of the $L_{2,3}$-emission band appears in the region where the $K\beta$-emission band has the small intensity on the low-energy side of its main peak β_1. From this comparison, we can conclude that the upper part of the valence band consists of both the $3d$ electrons of the Mn^{2+} ion and the $3p$ electrons of the S^{2-} ion (especially, the top of the valence band consists of the Mn^{2+} $3d$ electrons), and the lower part consists of the $3s$ electrons of the S^{2-} ion. Recently, such a band scheme has been made from the assignment of the optical absorption spectrum[26] of α-MnS and the Mn $K\beta_5$- emission band,[27] and is also consistent with the result of the energy-band calculation.[3] The energy separation between the $K\beta_1$-emission edge (2467.8 eV) and the K-absorption edge (2471.2 eV)[24] is 3.4 eV and this value is somewhat larger than the band gap 3.2 eV.[3] This discrepancy can be understood by the fact that the top of the valence band consists of the $3d$ states of the Mn^{2+} ion and the electronic transition from the d states to the $1s$ state of the S^{2-} ion is forbidden on the dipole selection rules.

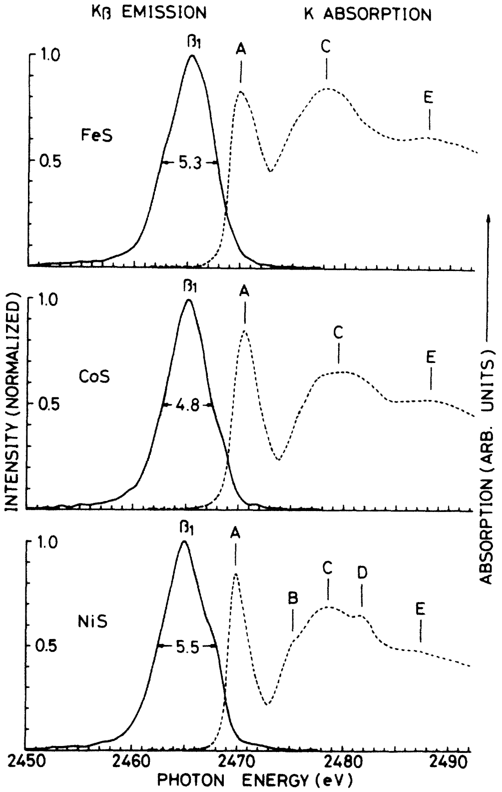

FIG. 3. $K\beta$-emission and K-absorption (Ref. 28) spectra of sulfur in FeS, CoS, and NiS.

B. FeS, CoS, and NiS

The sulfur $K\beta$-emission and K-absorption[28] spectra of FeS, CoS, and NiS are shown in Fig. 3. The $K\beta$-emission spectra as well as the K-absorption spectra are similar to one another. This seems to indicate that the p-like states in the valence and conduction bands of these metal sulfides are alike. The similar electronic states can be understood by the fact that these sulfides crystallize in the same crystal structure (NiAs structure). The $K\beta_1$-band edge overlaps with the K-absorption edge. This result indicates that these sulfides are metallike compounds, and is consistent with the experimental results that the electrical conductivity for FeS and NiS were metallic.[29,30] The K-absorption spectra are characterized by the first prominent peak A which becomes narrower from FeS to NiS.

Let us now compare the sulfur $K\beta$-emission and K-absorption spectra of NiS with the result of the theoretical band calculations.[4] In Fig. 4, the emission and absorption spectra are compared with the density of states for metallic NiS, where the intersection of the emission and absorption curves is tentatively associated with the Fermi energy in the density of states. The $K\beta_1$-emission band corresponds to the broad band (arising pre-

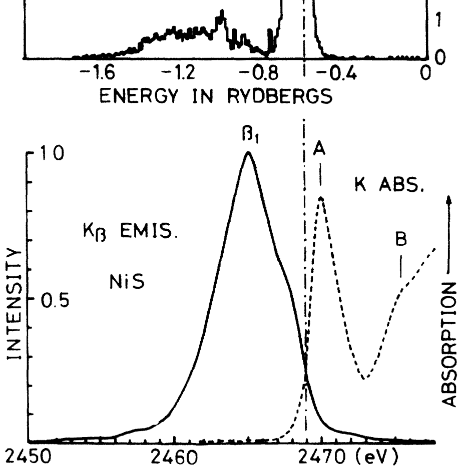

FIG. 4. $K\beta$ emission and K absorption (Ref. 28) of sulfur in NiS are compared with the density of states of metallic NiS (Ref. 4).

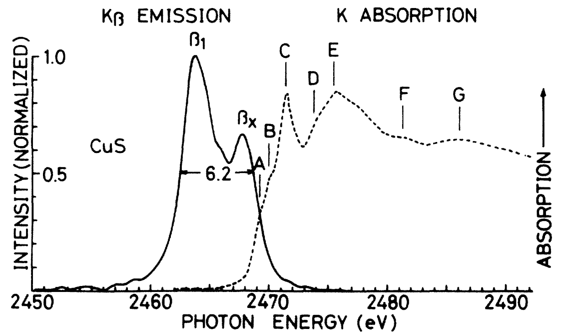

FIG. 5. $K\beta$-emission and K-absorption (Ref. 28) spectra of sulfur in CuS.

dominantly from the $3p$ states of sulfur) below the Fermi energy and the high-energy shoulder corresponds to the strong, sharp d band (arising from the $3d$ states of nickel) just below. Recently, this overlap of the S $3p$ bands and the d bands was indicated by White and Mott,[31] Koehler and White,[30] and Kasowski.[5] Moreover, the first absorption band A corresponds to the empty d band just above the Fermi energy. These occupied and unoccupied d bands rather ought to compare with the Ni $L\alpha$-emission and L_3-absorption spectra of NiS, respectively. Unfortunately, the L spectra lie in the region of long wavelengths (about 14.5 Å) and were not measured. They have not yet been reported.

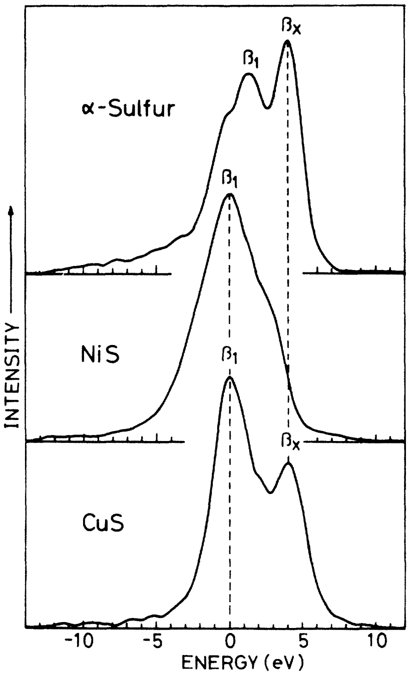

FIG. 6. Comparison of sulfur $K\beta$-emission spectra of α-sulfur, NiS, and CuS.

C. CuS

The sulfur $K\beta$-emission and K-absorption[28] spectra of CuS are shown in Fig. 5. The $K\beta$-band edge overlaps with the K-absorption edge. This indicates that CuS is a metallike compound, and is consistent with the metallic character of conductivity. The $K\beta$-emission spectrum consists of two characteristic peaks and is somewhat similar to the $K\beta$-emission spectrum from α-sulfur, although these spectra differ on the intensity (see Fig. 6). This similarity may be due to the fact that both CuS and α-sulfur have the bond S–S, because the $K\beta$-emission spectrum of α-sulfur can be fairly

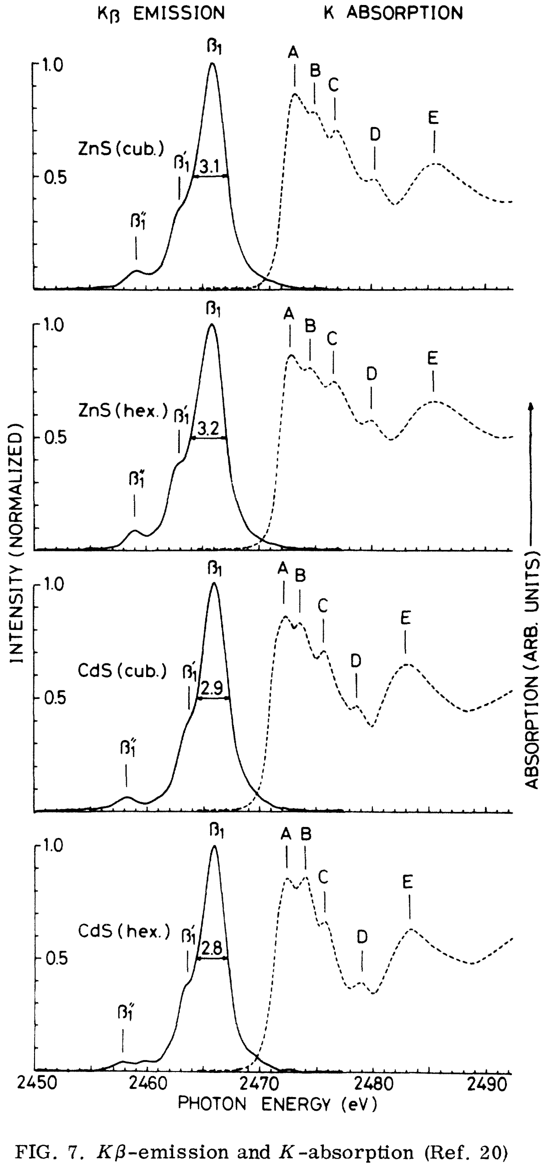

FIG. 7. $K\beta$-emission and K-absorption (Ref. 20) spectra of sulfur in two modifications (zinc-blende and wurtzite structures) of ZnS and CdS.

well accounted[32,33] for in terms of the molecular orbitals of the S_8 molecule (S–S = 2.05 Å).[34] Cupric sulfide (CuS) is a compound with Cu atoms states Cu^+ and Cu^{2+}, and with S atoms of two types: single S and radical S_2. The space group[35] is D_{6h}^4. The characteristic $K\beta$-emission spectrum probably consists of the overlap of the sulfur $K\beta$-emission spectra from the bonds Cu^+–S (= 2.19 Å),[35] Cu^{2+}–S (= 2.31 Å),[35] and S–S (= 2.05 Å).[35] However, the sulfur $K\beta$ spectrum of the bond Cu^+–S or Cu^{2+}–S has not yet been measured. Therefore, let us tentatively deduce the $K\beta$-emission spectrum of CuS in terms of the sulfur $K\beta$-emission spectra of α-sulfur and NiS (Ni–S = 2.38 Å).[35] A comparison of the sulfur $K\beta$-emission spectra of α-sulfur, NiS, and CuS is shown in Fig. 6, where the peak β_1 of NiS and the peak βx of α-sulfur are associated with two peaks β_1 and βx of CuS, respectively. The $K\beta$-emission spectrum of CuS seems to become somewhat similar to the overlap of the spectra of α-sulfur and NiS. From this comparison, we can deduce that the characteristic $K\beta$ spectrum of CuS consists of the overlap of the sulfur $K\beta$ spectra from the bonds Cu^+–S, Cu^{2+}–S, and S–S. In addition, the fine structure near the sulfur K-absorption edge of CuS is more complex than those of FeS, CoS, and NiS (see Fig. 3). This seems to support the viewpoint that the sulfur K-absorption spectrum of CuS consists of the overlap of the sulfur K-absorption spectra from the bonds Cu^+–S, Cu^{2+}–S, and S–S. Such a result has been found on the Cu L_3-absorption spectrum[36] of CuS.

D. ZnS and CdS

The sulfur $K\beta$-emission and K-absorption spectra[20] from two modifications of ZnS and CdS are shown in Fig. 7. The $K\beta$-emission spectra as well as the K-absorption spectra are alike among four different materials. Similar a result has been recently found on the sulfur $L_{2,3}$-absorption spectra[13,37] for CdS. These experimental results seem to indicate that the energy-band structures of cubic and hexagonal ZnS or CdS are alike. On the other hand, the arrangement of the atoms in the modifications is the same in the nearest neighbors and takes a small difference in the next-nearest neighbors, hence the band structures are supposed to be similar to each other. The similarity of the band structure of cubic and hexagonal ZnS has been indicated by Birman,[38] and by Bergstresser and Cohen[7] using the Birman correspondence; Γ_1, L_1, and L_3 (cubic) correspond to Γ_1, Γ_3 and Γ_5 (hexagonal), respectively; Γ_{15} (cubic) corresponds to Γ_6 plus Γ_1 (hexagonal). There is no doubt that the similar emission and absorption spectra from the modifications represent the similar energy-band structure. In addition, the similar $K\beta$-emission or K-absorption spectra of cubic (or hexagonal) ZnS and CdS can be understood in terms of the similarity of the calculated band structure.[7,9]

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