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Resonant photoemission study of pyrite-type NiS_2, CoS_2 and FeS_2

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The electronic structure of pyrite-type NiS_2, CoS_2, and FeS_2 has been studied by photoemission spectroscopy. From resonant photoemission studies and configuration-interaction cluster-model analysis of the spectra, NiS_2 is found to be a charge-transfer-type insulator, the band gap of which is formed between the occupied S $3p$ and the empty Ni $3d$ states. Cluster-model calculations indicate that the short Fe-S distance favors the low-spin ($S=0$) ground state in FeS_2 compared to the high-spin FeS. Resonant photoemission results indicate a sign of electron correlation in the nonmagnetic semiconductor FeS_2. [S0163-1829(96)02147-9]

Pyrite-type $3d$ transition-metal dichalcogenides exhibit a wide variety of electrical and magnetic properties:[1] FeS_2 is a semiconductor with a band gap of $E_g \simeq$ 0.9 eV;[2] CoS_2 is metallic and orders ferromagnetically below $T_c \simeq$ 120 K;[3] NiS_2 is an antiferromagnetic insulator with $E_g \simeq$ 0.3 eV (Ref. 4), and $T_N \simeq$ 40 K.[5] The transition-metal ions in these compounds are divalent and have a tendency to take low-spin states: FeS_2 (d^6) is nonmagnetic ($S=0$) and CoS_2 (d^7) has a saturation moment of $0.85\mu_B$/Co (Ref. 3) close to that of $S=1/2$. NiS_2 (d^8) is a high-spin ($S=1$) compound but the d^8 configuration cannot take a lower spin state in a cubic crystal field.[6] $NiSe_2$ (Ref. 7) and CuS_2 (Ref. 8) are Pauli-paramagnetic metals. One-electron band models have been proposed to explain these properties:[1,9] Between the empty S $3p$ band consisting of the $p\sigma^*$ antibonding orbital of the $(S_2)^{2-}$ molecule and the occupied S $3p$ band of the remaining $(S_2)^{2-}$ orbitals, a relatively wide metal $3d$ (e_g) band and a narrow $3d$ (t_{2g}) band are located. In FeS_2, the t_{2g} band is full and the e_g band is empty, leading to the nonmagnetic, insulating behavior. In CoS_2, the e_g band is occupied by one electron per Co and polarized ferromagnetically. NiS_2 is insulating in spite of the half-filled e_g band, and is therefore considered to be a Mott insulator.[1]

According to the current interpretation of photoemission spectra, the band gaps of late $3d$ transition-metal compounds such as NiO and NiS are of the anion p-to-metal d charge-transfer type.[10,11] Metal-insulator transitions in this type of compounds are thus attributed to the closing of a charge-transfer-type p-d gap rather than that of a Mott-Hubbard-type d-d gap.[12] Recent analysis of the metal core levels using the configuration-interaction (CI) cluster model has indeed shown the charge-transfer nature of the band gap in NiS_2.[13,14] Recently, angle-resolved photoemission studies have been performed for NiS_2 and $NiS_{2-x}Se_x$ and their electronic stuctures in the vicinity of the Fermi level across the metal-insulator transition have been studied with high energy resolution.[15] In this paper, we report the results of photoemission studies of pyrite-type NiS_2, CoS_2, and FeS_2 and discuss their overall electronic structures on the basis of cluster-model analyses.

Single crystals of NiS_2 and CoS_2 were grown by the vapor transport method. FeS_2 samples were a natural mineral. Photoemission measurements were performed at beamline BL-2 of the Synchrotron Radiation Laboratory, Institute for Solid State Physics, University of Tokyo. Measurements were also made using a spectrometer equipped with a He discharge lamp ($h\nu=$ 21.2 eV and 40.8 eV). The total resolution was ~0.5 eV and ~0.3 eV, respectively, for the synchrotron radiation and He lamp experiments. Clean surfaces were obtained by scraping *in situ* with a diamond file, and the measurements were made at room temperature. The base pressure of the spectrometers was $\sim 1\times 10^{-10}$ Torr.

Photoemission spectra of FeS_2, CoS_2, and NiS_2 are shown in Figs. 1–3. They all show a prominent peak at 1–2 eV below the Fermi level (E_F). From a comparison of spectra taken at $h\nu=$ 21.2 eV and 40.8 eV, where the photoionization cross section of the S $3p$ states is enhanced compared to the transition-metal $3d$ states and is suppressed due to a Cooper minimum at $h\nu\sim$ 50 eV (not shown), respectively, we were able to identify the S $3p$ band to be located 1–9 eV below E_F. The origin of the peak at 1–2 eV is then attributed to transition-metal $3d$ states. The peak is the narrowest in FeS_2, where only the t_{2g} band is occupied. In going from FeS_2 to CoS_2 to NiS_2, the peak becomes broader and a

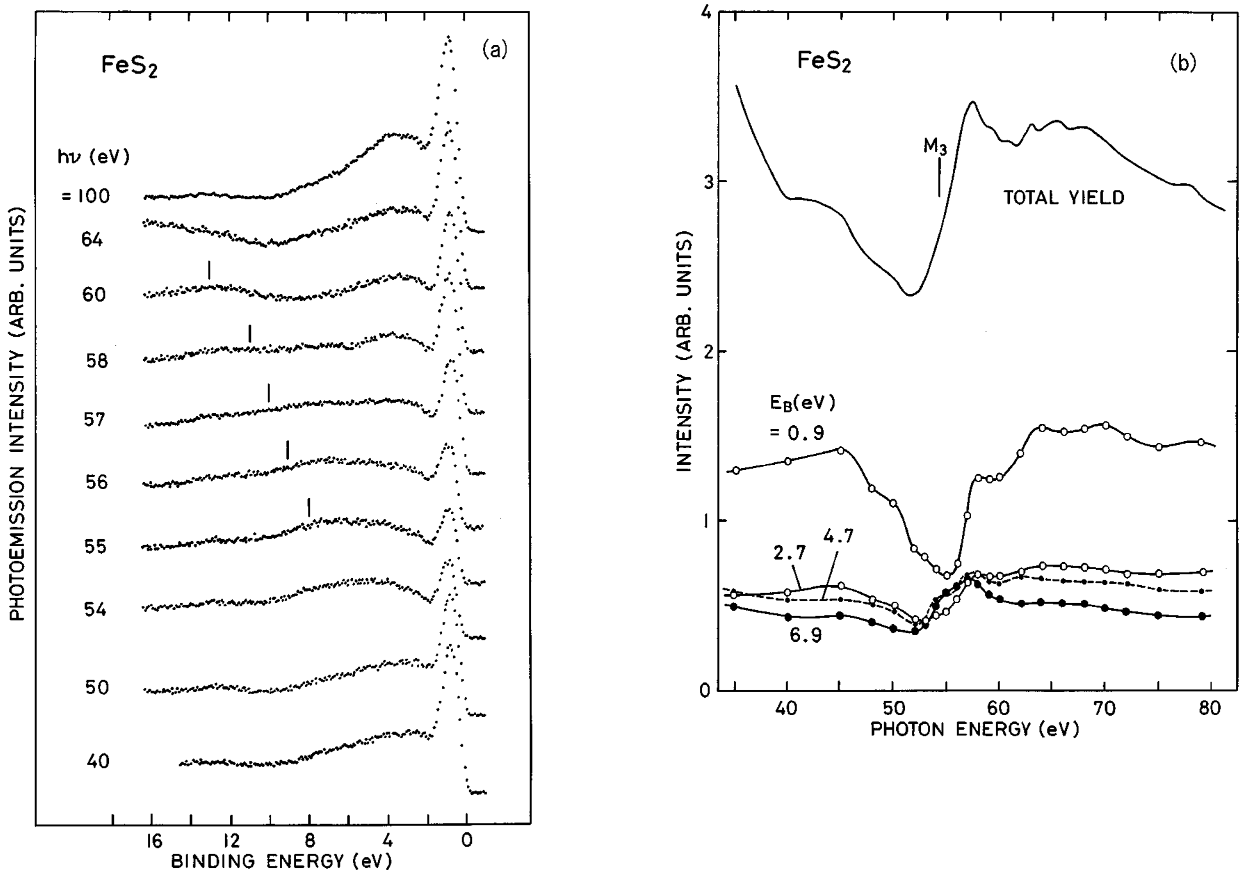

FIG. 1. Photoemission spectra of FeS_2 in the Fe $3p \rightarrow 3d$ core-absorption region. The vertical lines mark the kinetic energy of the $M_{2,3}M_{4,5}M_{4,5}$ Auger peak, indicating that the enhancement of the satellite is not due to an overlap of the Auger emission.

weak shoulder appears on its lower binding energy side, i.e., near E_F, as previously reported.[16] The evolution of the latter feature with transition-metal atomic number represents the successive filling of the e_g band by the added electrons. The broadening of the t_{2g} peak is interpreted as due to its exchange splitting band as the spin polarization of the d (e_g) band is increased. For such an interpretation to be valid, however, because the measurements have been done above T_c or T_N, the spin polarization should persist above T_c or T_N on the short time scale of photoemission spectroscopy ($\sim 10^{-15}$ sec) even in the paramagnetic state as in the ''local band picture.''[17]

The appearance of the broad satellite features at 6–10 eV is also beyond the ordinary band model. This satellite is most clearly seen in NiS_2 and shows an enhancement for photon energies above the Ni $3p \rightarrow 3d$ core-absorption threshold ($h\nu \sim 66$ eV), whereas the main band within ~ 5 eV of E_F shows antiresonace behavior at the threshold, as can be seen from the constant-initial-state spectra shown in Fig. 3(b). We therefore interpret the satellite primarily due to d^7 final states and the main band as due to $d^8\underline{L}$ final states ($\underline{L}$: a ligand hole) as in the case of NiO (Ref. 10) and NiS.[11] That is, the highest occupied states in NiS_2 are S $3p$-like rather than Ni $3d$-like and the band gap is of the p-to-d charge-transfer type rather than the d-d Mott-Hubbard type. This view is supported by the cluster-model analysis described below.

The fact that the resonant enhancement in the satellite region is observed in every compound [Figs. 1(b)–3(b)] indicates that electron correlation is important in every compound including the nonmagnetic insulator FeS_2. This means that FeS_2 is not simply an ordinary band insulator but is a correlated insulator at least qualitatively like FeSi (Ref. 18) or $LaCoO_3$,[19] in which temperature-induced paramagnetism is observed. However, the band gap of FeS_2 ($\simeq 0.9$ eV) is much larger than those of FeSi ($\simeq 0.05$ eV) and $LaCoO_3$ ($\simeq 0.2$ eV),[20] making the system nonmagnetic at accessible temperatures. Figures 1–3 show that in going from NiS_2 to CoS_2 to FeS_2, the resonance behavior of the satellite above the $3p \rightarrow 3d$ threshold becomes less prominent relative to the (anti)resonance behavior of the main band as in $3d$ transition-metal oxides.[21,10]

In order to confirm the charge-transfer nature of the band gap in NiS_2 and to gain more insight into the electronic structure, we have analyzed the photoemission spectra by a standard CI calculation on the $(NiS_6)^{10-}$ cluster model as has been done for NiS.[11] The ground-state wave function of the cluster is given by a linear combination of the d^8, $d^9\underline{L}$, and $d^{10}\underline{L}^2$ configurations and the photoemission final states by those of the d^7, $d^8\underline{L}$, and $d^9\underline{L}^2$ configurations. The model contains a few adjustable parameters, namely, the on-site d-d Coulomb energy U, the p-to-d charge-transfer energy $\Delta \equiv \langle d^9\underline{L}|H|d^9\underline{L}\rangle - \langle d^8|H|d^8\rangle$, and the d-p transfer integrals $(pd\sigma)$ and $(pd\pi)$, where we have assumed $(pd\sigma)/(pd\pi) = -2.2$ as before.[22] Here, Δ and U are defined with respect to the center of gravity of each multiplet. Atomic values are used for Racah B, C parameters.[10,11] For simplicity, the S $3s$ orbitals have been neglected in the basis set;[11] instead, effects of hybridization between the S $3s$ and

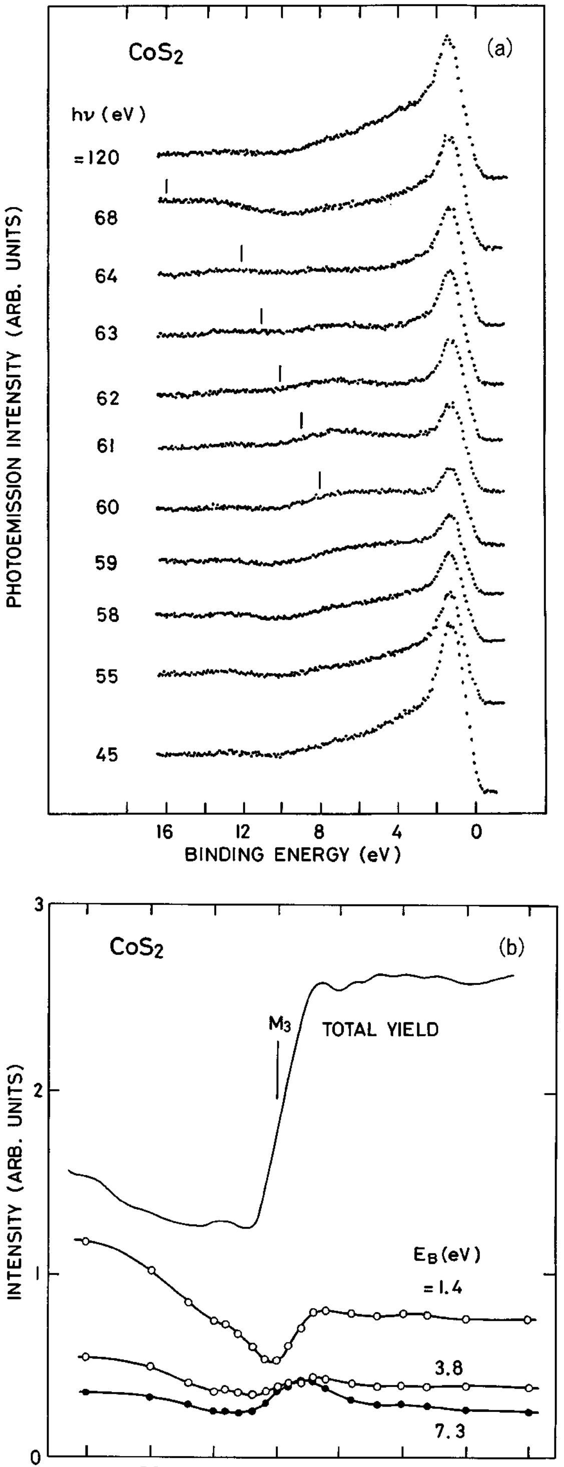

FIG. 2. Photoemission spectra of CoS_2 in the Co $3p \rightarrow 3d$ core-absorption region. The same as Fig. 1.

Ni $3d$ (e_g) orbitals are incorporated through a crystal-field parameter $10Dq \sim [\sqrt{3}(sd\sigma)]^2/(\Delta+\varepsilon_{3p}-\varepsilon_{3s})$ in the initial state and $10Dq \sim [\sqrt{3}(sd\sigma)]^2/(\Delta-U+\varepsilon_{3p}-\varepsilon_{3s})$ in the final state of photoemission, where $(sd\sigma)/(pd\sigma)=1.1$ and the S $3p$-$3s$ energy difference $\varepsilon_{3p}-\varepsilon_{3s}=$ 10 eV.[11] Figure 4 shows the best fit to the $h\nu=$ 40.8 eV spectrum obtained with $\Delta=1.8$ eV, $U=3.3$ eV and $(pd\sigma)=1.5$ eV, typical errors being ± 0.2 eV for U and Δ and ± 0.05 eV for $(pd\sigma)$.

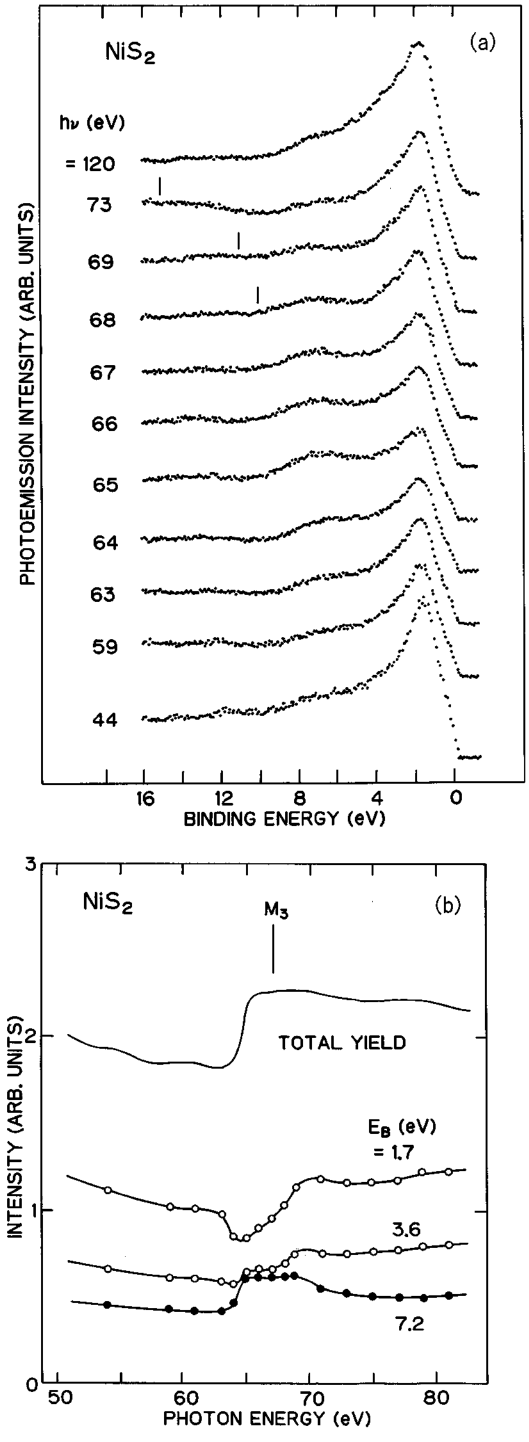

FIG. 3. Photoemission spectra of NiS_2 in the Ni $3p \rightarrow 3d$ core-absorption region. The same as Fig. 1.

At this photon energy, the S $3p$ cross-section is negligibly small compared to Ni $3d$ and therefore has been neglected in the analysis. Using this parameter set, the $d^8\underline{L}$-like main peak, which is broader than that of NiS, has been reproduced as shown in Fig. 4. However, the discrepancy between theory and experiment at 3–6 eV could not be eliminated in the present calculation. This indicates that a more realistic model which takes into account the characteristic feature of the pyrite-type structure, namely, the presence of the S_2 molecules[13] would be necessary. Also, the strong Ni-S

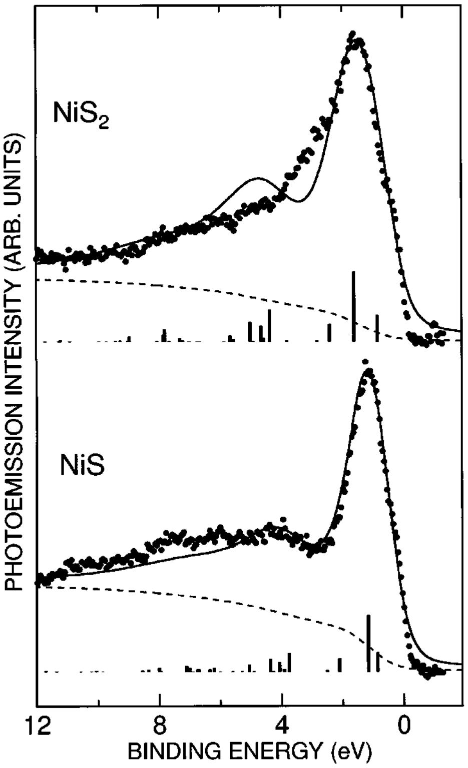

FIG. 4. Photoemission spectra of NiS$_2$ and NiS compared with configuration-interaction (CI) cluster-model calculation. The calculated line spectrum has been broadened and superposed on the integral background (dashed curve). The spectrum of NiS is taken from Ref. 11.

covalency will make the intercluster hybridization important, possibly making it necessary to go beyond the single-impurity cluster model.

In order to obtain the wider $d^8\underline{L}$ main peak in NiS$_2$ than in NiS, the Δ value for NiS$_2$ had to be chosen smaller and the $(pd\sigma)$ value larger than those for NiS, for which we use $\Delta=2.2\pm0.2$ eV, $U=3.2\pm0.6$ eV, and $(pd\sigma)=1.3\pm0.05$ eV, as shown in Fig. 4. Considering the systematic decrease of Δ and the increase of U with cation atomic number (by $\sim$0.5 eV for Δ and by $\sim$0.3 eV for U, for a unit increase of the atomic number),[18] we estimate $\Delta\simeq2.3$ eV and $U\simeq3.0$ eV for CoS$_2$ and $\Delta\simeq2.8$ eV and $U\simeq2.8$ eV for FeS$_2$. This locates CoS$_2$ and FeS$_2$ closer to the boundary between the charge-transfer and Mott-Hubbard regimes.

In order to explain the contrasting behaviors of low-spin FeS$_2$ and high-spin FeS, we have calculated the lowest energies of the $S=0$ and $S=2$ states for the $(\mathrm{FeS}_6)^{10-}$ cluster model. Following the results of NiS$_2$ and NiS, we have assumed that U and Δ are smaller for FeS$_2$ than for FeS by $\sim$0.7 eV and $\sim$0.5 eV, respectively. The $(pd\sigma)$ of FeS$_2$ has been estimated to be 2.2 eV from that of NiS$_2$ using the relationship $(pd\sigma)\propto r_d^{1.5}/d_{M-\mathrm{S}}^{3.5}$, where r_d is the ''atomic radius'' of the metal ion,[22] $r_d=$ 0.71 A for NiS$_2$ and 0.80 A for FeS$_2$, and $d_{M-\mathrm{S}}$ is the metal-sulfur atomic distance, $d_{M-\mathrm{S}}=$ 2.40 A for NiS$_2$ and 2.26 A for FeS$_2$.[23] Likewise, the $(pd\sigma)$ of FeS has been estimated to be 1.4 eV from that of NiS using $d_{M-\mathrm{S}}=$ 2.38 A (NiS) and 2.45 A (FeS). Thus in FeS$_2$ the low-spin state is calculated to be lower than the high-spin state by 1.5 eV, while in FeS the high-spin state is calcuted to be lower than the low-spin state by 0.6 eV. Although these absolute values may not be accurate due to the various uncertainties introduced in the parameter estimates, it can be concluded that the cluster-model calculations well explain the low-spin and high-spin behaviors in FeS$_2$ and FeS primarily as due to the larger $(pd\sigma)$ arising from the smaller Fe-S distance in FeS$_2$ than in FeS.

In conclusion, we have studied the electronic structures of NiS$_2$, CoS$_2$, and FeS$_2$ by photoemission spectroscopy and subsequent cluster-model calculations. The photoemission spectrum calculated using the cluster model has reproduced the gross features of the measured spectra but there remains a discrepancy between the theoretical and experimental spectral line shapes. Probably the peculiar crystal structures of the pyrite-type compounds containing the molecules and/or the intercluster hybridization would have to be considered in order to better understand the interesting physical properties of the pyrite-type compounds.

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