Reflectivity Spectra and Optical Constants of Pyrites (FeS₂, CoS₂ and NiS₂) between 0.2 and 4.4 eV

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Near-normal incidence reflectivity spectra of pyrite type compounds (FeS_2, CoS_2 and NiS_2) have been measured for photon energies between 0.2 and 4.4 eV. By using Kramers-Kronig relations, optical constants (n and k) and absorption coefficient have been calculated. Absorption spectra of FeS_2 and CoS_2 thus obtained are in good agreement with those directly measured on thin films. Absorption edge of NiS_2 is located around 0.3 eV, which is very close to 0.37 eV obtained from the absorption spectrum of a bulk crystal. Absorption spectra of FeS_2 and CoS_2 in the energy region of the measurements are interpreted in terms of the band to band transition from the occupied t_{2g} states to the unoccupied e_g states derived from the transition metal ions of these compounds.

In recent years, there has been a considerable interest in the transition metal dichalcogenides with the pyrite type crystal structure, in which 3d electrons are in an intermediate state between localized and itinerant limits.

In order to get more distinct pictures on the electronic structures especially in the vicinity of Fermi level, the present author and his colleagues have been working on optical and magneto-optical studies of these compounds.[1-3,7]

Optical constants of pyrites were reported by Bither et al. for photon energies 0.5 to 6 eV.[4] However, the energy region of their measurements was insufficient for detailed identification of electronic structures of these materials. To extend the energy range to higher energies, VUV spectra were measured by using the synchrotron radiation, which have been reported elsewhere.[3] Data of Bither et al. were also insufficient for infrared region: Their spectra failed to locate the position of absorption edge in NiS_2. The intention of this letter is to provide more precise reflectivity spectra of pyrites for photon energies between 0.2 and 4.4 eV and to discuss the electronic structures near the Fermi level.

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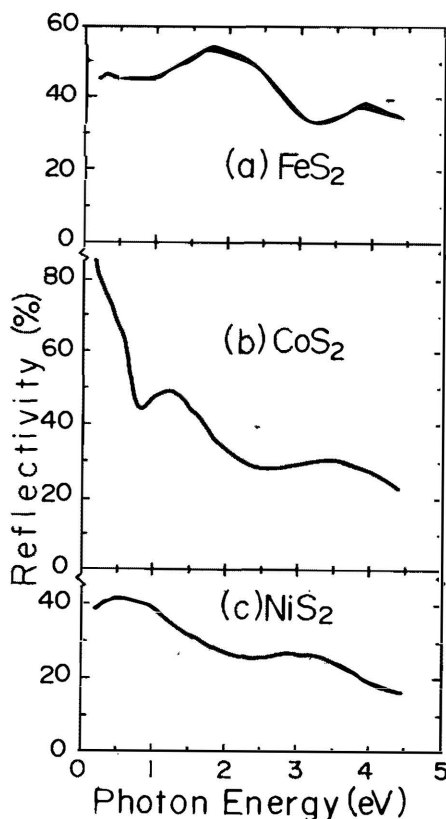
Single crystals of FeS_2, CoS_2 and NiS_2 have been prepared by chemical vapour transport reaction using chlorine as a transporting agent. The growth-surfaces of the obtained crystals showed mirror-like lusters. The surfaces were analyzed by X-ray Laue photography and were determined to have {100} crystal plane for FeS_2 and {111} for the other two. The crystal surfaces were 2–4 mm² in area.

Prior to reflectance measurements, as-grown surfaces were lightly etched with dilute HCl for a few minutes followed by the ultrasonic lince in the de-ionized water bath.

Near-normal incidence reflectivity spectra for 0.5–4.4 eV region were measured by using a specially designed double-beam reflectance spectrometer, the details of which will be published elsewhere.[5] The spot size of the light beam on the crystal surface was typically 0.2×0.5 mm². For infrared region below 0.5 eV, an infrared reflectance spectrometer (JASCO MSM 25C) was employed. This spectrometer also enables the reflectivity measurements of small crystals since the light spot at the beam focal plane is as small as 0.3 mm in diameter.

Reflectivity spectra of FeS_2, CoS_2 and NiS_2 are shown in Fig. 1. For FeS_2 the overall spectral features are very close to those reported by Schlegel and Wachter,[6] although some discrepancies exist in the infrared

Fig. 1. Reflectivity spectra of pyrites at room temperature. (a) FeS_2, (b) CoS_2 and (c) NiS_2.

Fig. 2. Optical constants of pyrites calculated from reflectivity spectra shown in Fig. 1. Solid curves represent n and dotted curves k. (a) FeS_2, (b) CoS_2 and (c) NiS_2.

region. The spectrum of CoS_2 between 0.5 and 4.4 eV was almost the same with the one reported in my previous report.[1] For infrared region below 0.5 eV reflectivity increases strongly as the photon energy decreases, and reaches as much as 84% at 0.2 eV. This increase of reflectivity has been attributed to the Drude tail associated with the intraband transition of conduction electrons.[7] The spectrum of NiS_2 below 2 eV is completely different from the one reported in ref. 4, in which reflectivity reaches 60% at around 0.6 eV. Repeated experiments confirmed that the reflectivity of NiS_2 does by no means get such a large value below 2 eV.

These spectra were connected with the VUV data[3] for Kramers-Kronig analysis, from which optical constants n and k (illustrated in Fig. 2) and absorption coefficient (shown in Fig. 3) were calculated.

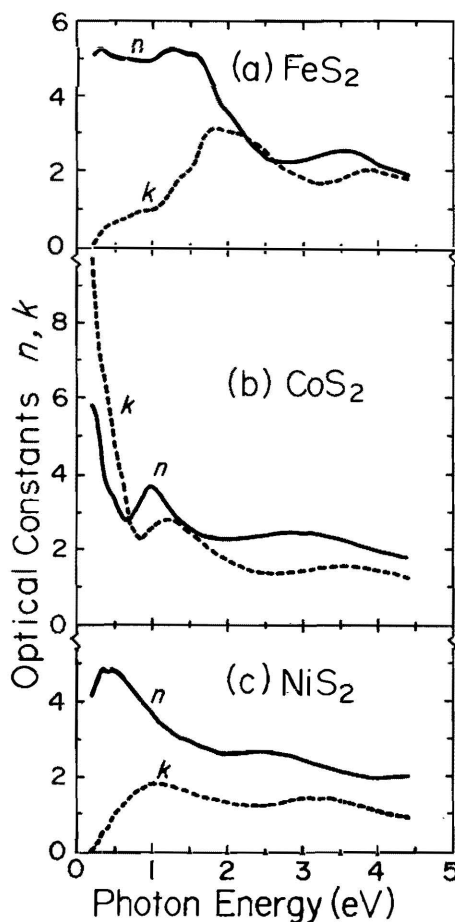Absorption spectra of thin FeS_2 and CoS_2 films prepared by using the close-spacing CVD

technique as descibed in ref. 1 are also included by dotted lines in Fig. 3. Close resemblance is seen between the absorption spectra deduced from the reflectivity and those obtained from the direct measurements on thin films. The absorption edge of FeS_2 was determined to be 0.9 eV by the extrapolation of the absorption curve above 1 eV to the abscissa of the graph, as shown by the broken line. This value agrees with the one reported by Kou et al.[8] However, there exists an absorption tailing below 1 eV in the present result, which may be due to some kind of crystalline defect such as sulfur vacancy.

Absorption spectrum of NiS_2 obtained by the Kramers-Kronig analysis shows a well defined absorption edge at 0.3 eV, which is in
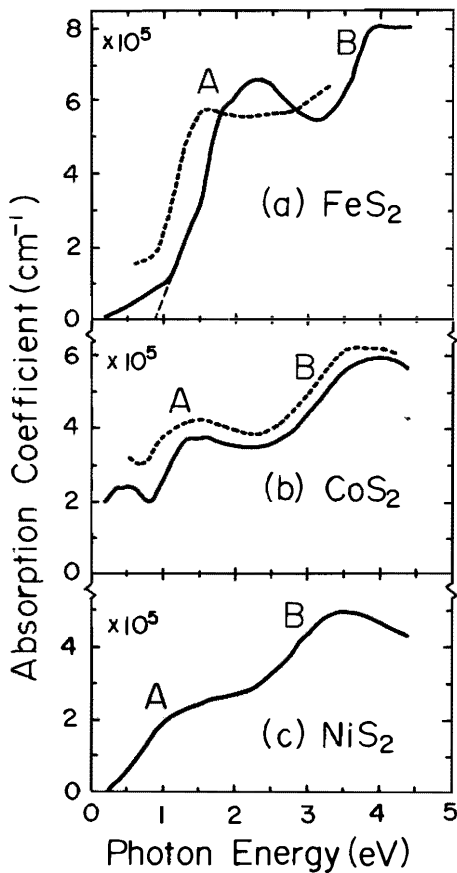
Fig. 3. Absorption spectra of pyrites. Solid curves represent those obtained from the Kramers-Kronig analysis and dotted curves those measured on thin films. (a) FeS_2. (Broken line denotes the extrapolation to get the absorption edge.) (b) CoS_2. (c) NiS_2.

from Fig. 3 that the absorption intensity of the peak A becomes weaker when one proceeds from FeS_2 to CoS_2 and NiS_2: This tendency corresponds to the filling of the $e_g d$ band in the above series.

Optical absorption spectrum due to band to band transition can be expressed in terms of the joint density of states (JDOS) and the transition probabilities between occupied and unoccupied states. If spectral dependence of the transition probability is neglected a rough estimate of absorption spectrum can be obtained from the JDOS spectrum. The latter has been estimated by using the DOS curves obtained by the band calculation.[10] In Fig. 4 are shown the JDOS curves for FeS_2, CoS_2 and NiS_2 so calculated.

In FeS_2 and CoS_2 one can find considerable similarity between the overall features of the JDOS curves and those of the observed ab-
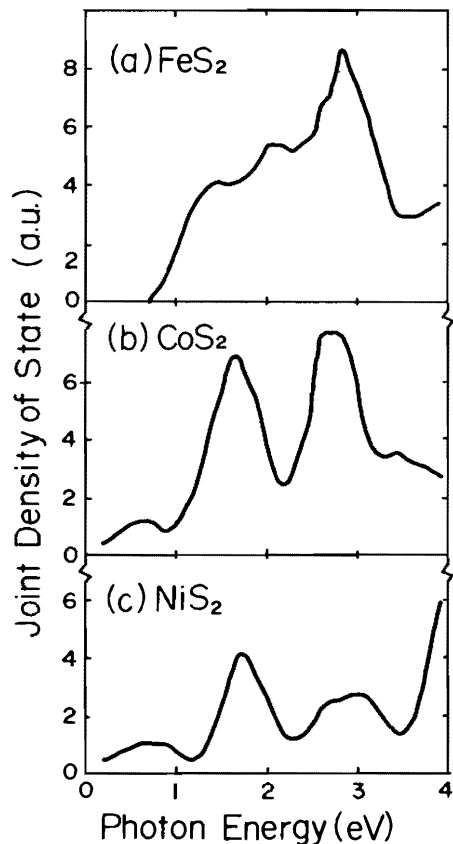
close agreement with 0.37 eV obtained from the absorption spectrum of a bulk crystal.[9] This indicates that the present results on NiS_2 are more reliable than those reported in ref. 4.

The rest of this letter is devoted to a brief interpretation of the absorption spectra of pyrites. According to the band structure calculated by Bullett[10] the occupied $t_{2g}d$ manifolds in FeS_2 are separated from the unoccupied $e_g d$ states by a clear gap of 0.7 eV. Absorption band A may be assigned to the optical transition across this gap. The $e_g d$ states make a broad band through a hybridization with $3p$ orbitals of the sulfur ion. The bottom part of the band shows a narrow peak in the density of state (DOS) spectrum with strongly d-like nature, while the upper part shows a broad p-like character. It can be seen

Fig. 4. Joint density of states (JDOS) spectra of FeS_2, CoS_2 and NiS_2 estimated by the present author from the density of states curves reported by Bullett.[10]

sorption spectra; agreements are satisfactory particularly in the low-energy region where contribution from a narrow high DOS peak of t_{2g} band combined with a relatively narrow DOS peak in the bottom of e_g band dominates. For peak B agreements are rather poor; the calculated peak position seems to be shifted by about 1 eV from the observed one. The peak B can be assigned to a transition from the t_{2g} band to the upper part of the e_g band, in which p-like character dominates. The discrepancy between the observed and calculated spectra around this peak may be attributed to a crudeness of the assumption that the same transition probability applies to both d to d and d to p transitions, as well as to a reduced accuracy in the calculation of higher bands.

For NiS$_2$, however, the calculated JDOS curve fails to account for the observed absorption spectrum. It has been pointed out that NiS$_2$ is a Mott insulator due to a strong correlation effect.[11] One electron band picture is, therefore, no more valid in this material especially in the vicinity of the Fermi level. Instead, the absorption spectrum should be interpreted in terms of the Mott-Hubbard picture including the correlation effects.

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