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Reflectivity and Absorption Spectra of CoS_2

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Reflectivity spectra of a single crystal of a metallic ferromagnet CoS_2 were measured between 0.5 and 5.0 eV at room temperature in air. Photon energy dependencies of optical constants n and k, an absorption coefficient α and real and imaginary parts of dielectric constant ε $(=\varepsilon'+i\varepsilon'')$ have been obtained from the Kramers-Kronig analysis of the reflectivity data. Absorption spectrum of a thin polycrystalline film was also measured, which proved to be in quantitative agreement with the one deduced from the reflectivity spectrum. From the curve of ε' the free electron plasma frequency ω_p was located at 0.8 eV from which number of free electrons was evaluated to be 0.5 per a CoS_2 molecule.

§1. Introduction

Cobalt disulfide, which crystallizes in the pyrite structure, is known to be a ferromagnet ($T_c \sim 120$ K) with a metallic conduction.[1] In recent years it has been drawing much attention as an example to which the theory of itinerant electron magnetism is applied.[2] Nevertheless, little is known about its electronic band structures except for the qualitative ones.[3–5]

For quantitative discussion of electronic structures of solids optical studies are known to be helpful. However, only a few optical data[6–8] have been reported on CoS_2. The authors, therefore, started optical studies of this material; reflectivity, absorption and magneto-optical measurements.

The present paper reports on studies of reflectivity spectrum of a single crystal and absorption spectrum of a polycrystalline film.

§2. Experimentals

2.1 Sample preparation

Single crystals of CoS_2 were grown by the chemical vapor transport technique with chlorine as a transporting agent. Starting materials were CoS_2 powder which had been prepared by the solid-phase reaction of a mixture of constituent elements with a few percent excess of sulfur. The charges together with 0.2–0.5 atm chlorine gas were sealed in a fused silica ampoule which had been evacuated to 10^{-5} mmHg. The ampoule was placed in a two-zone furnace with $T_1=800°C$ and $T_2=725°C$. In the first few days of the transporting process, temperatures of two zones were changed periodically between 800°C and 725°C following the method described by Bouchard;[9] then they were kept unchanged for the rest of the process.

Single crystals grown were 3–5 mm in size with mirror-like surfaces. Their predominant planes were determined to be {111} by the X-ray Laue method. These crystals were rinsed with clean water in an ultrasonic bath to get rid of chlorides deposited on their surfaces during the transporting process, before mounting on a sample-holder for the reflectivity measurement. Reflectivity was measured on the {111} surface.

Thin polycrystalline films were prepared by means of the close-spacing CVD (chemical vapor deposition) method, which had been successfully applied to the growth of $CuFeS_2$ films.[10] The source powder of CoS_2 was prepared by crushing as-grown single crystals produced by the chemical transport technique described above. Some kind of chlorides included in the as-grown crytals become transporting agent of CVD. The source powder was placed in a graphite crucible heated by an IR lamp up to 450°C. The crucible was covered by a fused silica substrate which was also heated to 360°C by another lamp. The spacing between the source and the substrate was about 1 mm. The deposition was carried out in an evacuated fused silica reaction tube. The heating duration was 5–10 minutes.

Transparent thin films were obtained. Thickly deposited films were analyzed by the X-ray diffractometer and were found to be polycrystalline CoS_2 with an orientation preference of {100} plane parallel to the substrate. As regards thinner films only the strongest (200) reflection lines could be detected. Thickness of the films were determined by using an interference microscope.

2.2 *Reflectivity measurement*

Nearly normal incidence reflectivity spectra for photon energies between 0.5 and 5 eV were measured at room temperature in air by using a microcomputer-controlled spectrometer system equipped with a specially designed reflectance attachment, details of which have been reported elsewhere.[11,12] Calibration of the absolute value of reflectivity was performed by replacing the sample by a vacuum-deposited Al or Ag mirror. Data were recorded on a floppy disk file and processed by the microcomputer.

In our measuring system, however, some ambiguity is inevitably introduced for photon energies higher than 4 eV by surface deterioration of the sample as well as of used mirrors due to oxidation. For photon energies between 4 and 5 eV we borrowed the data of VUV (vacuum ultraviolet) reflectivity measured by using the synchrotron radiation.[13]*

§3. Results

Figure 1 is a reflectivity spectrum of the CoS_2 single crystal at room temperature. The spectrum is characterized by a steep rise of reflectivity below 0.8 eV and two broad maxima observed around 1.2 and 3.5 eV.

Optical absorption spectrum of the thin CoS_2 film was measured by using a Cary-14 spectrophotometer at room temperature. In Fig. 2 is shown a typical absorption spectrum of the film by a solid curve. The thickness of the film used for the measurement was 450 Å.

In Fig. 3 are illustrated spectra of optical

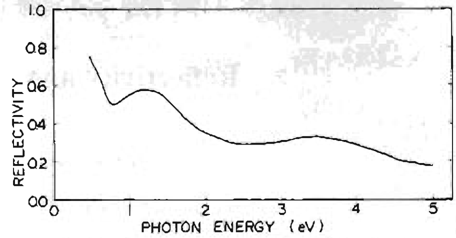

Fig. 1. Reflectivity spectrum of a CoS_2 single crystal at room temperature.

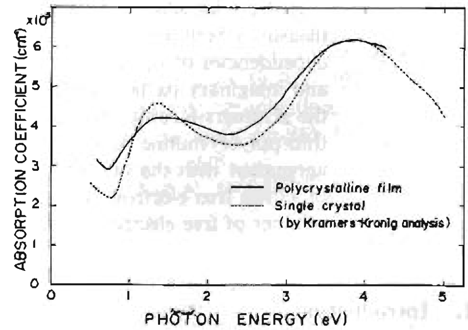

Fig. 2. Absorption spectra of CoS_2; Solid curve:—that of a thin polycrystalline film measured directly. (Thickness=450 Å). Dotted curve:—that calculated from the reflectivity spectrum of a single crystal.

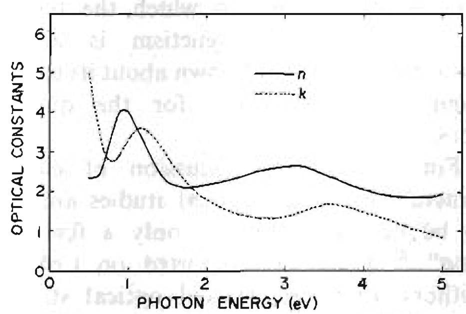

Fig. 3. Spectra of optical constants *n* and *k* of CoS_2 deduced from the reflectivity spectrum. Solid curve:—*n*. Dotted curve:—*k*.

constants *n* and *k* calculated from the Kramers-Kronig analysis[14] of the reflectivity data. This analysis was performed by using an IBM-370 computer. For application of the Kramers-Kronig relation it is necessary to extrapolate the data to energies outside the region of measurement. Fortunately, for energies above 4 eV the VUV spectrum was available up to 30 eV.[13] For lower energy side ($h\nu < 0.5$ eV) a linear relation up to unity was assumed for simplicity.

The absorption coefficient α was calculated from the extinction coefficient *k* by

* The sample used for the VUV measurement was not the same used in this study but one obtained by us at the same time in the same ampoule.

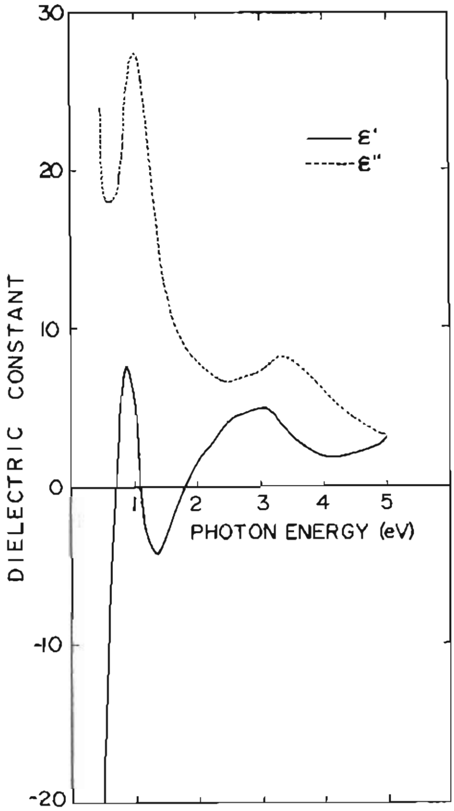

Fig. 4. Spectra of the dielectric constant of CoS_2 Solid curve:—real part (ε'). Dotted curve:—imaginary part (ε'').

$$\alpha = 2\omega k/c,$$

and is illustrated in Fig. 2 by a dotted curve. Quantitative agreement of the solid and the dotted curves can be seen.

Real and imaginary parts of the dielectric constant $\varepsilon = \varepsilon' + i\varepsilon''$ were also calculated and illustrated in Fig. 4 by solid (ε') and dotted (ε'') curves.

§4. Discussions

In the first place, it is observed in Fig. 4 that ε' crosses zero around 0.8 eV with positive gradient. This energy can be associated with a free-electron plasma frequency ω_p of this material, which is related to the number of free electrons n_f by an equation,

$$\omega_p^2 = \frac{4\pi n_f e^2}{m\varepsilon_{eff}(0)}, \qquad (1)$$

where e is the electron charge, m the free electron mass and $\varepsilon_{eff}(0)$ the effective dielectric constant which is evaluated by the sum rule,

$$\varepsilon_{eff}(0) = 1 + \frac{2}{\pi}\int_0^\infty \frac{\varepsilon''(\omega')}{\omega'} d\omega'. \qquad (2)$$

From eq. (2) we obtain $\varepsilon_{eff}(0) = 25.5$, using ε'' for energies between 0.5 and 30 eV deduced from the reflectivity using the VUV data.[13] Using the value of $\varepsilon_{eff}(0)$ and the observed value of ω_p we get from eq. (1) $n_f = 1.17 \times 10^{22}$ cm^{-3}, which corresponds to 0.5 electron per a CoS_2 molecule. This value is in good agreement with the one obtained from the Hall effect measurements, 0.53–1.1.[15] This can be intepreted that among seven $3d$ electrons derived from each Co atom nearly one electron acts as a free electron; i.e. the Fermi level lies in the e_g-band.

In the next place, two absorption maxima around 1.4 and 3.8 eV seen in the absorption curves of Fig. 2 will be assigned to interband transitions from the filled t_{2g}-band to the empty portion of e_g-band and/or to other conduction band states. These absorption peaks may be related to the broad absorption structure A of the X-ray K-absorption spectrum, although it was not resolved into two peaks due to poor resolution.[8]

Finally, we give a brief remark on the temperature dependence of the reflectivity spectrum. Since CoS_2 is ferromagnetic below T_c($\sim$120 K) an effect of the magnetic order on the optical spectrum was expected. However, no substantial change has been observed in our preliminary temperature dependence measurement, although a slight variation of the structure was found in the vicinity of the reflectivity dip around 0.8 eV.

§5. Conclusion

Reflectivity and absorption spectra of CoS_2 have been studied. Absorption spectrum deduced from the reflectivity was in good agreement with the one measured directly on a thin film; two peaks were observed around 1.4 and 3.8 eV.

From the curve of ε' obtained from the Kramers-Kronig analysis the free electron plasma frequency was determined to be 0.8 eV, from which the number of free electrons per a CoS_2 molecule was evaluated as 0.5 by using a calculated value of $\varepsilon_{eff}(0) = 25.5$.

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