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An optical absorption study of RuS₂ single crystals

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Abstract. The optical absorption study of synthetic RuS₂ single crystals grown in tellurium fluxes is reported over a temperature range from 4.2 K to 300 K. The data are fitted to several expressions for the shape of the absorption edge, with the best fit being to that expected for indirect allowed transitions. The indirect band gaps at various temperatures are determined. The temperature dependence is analysed by the Varshni equation and an empirical expression proposed by O'Donnell and Chen. The parameters that describe the temperature dependence of the energy gap of RuS₂ are evaluated. At temperatures lower than 100 K, several features which occur below the absorption edge are superposed on the absorption curve. The origin of these features is discussed.

1. Introduction

RuS₂ belongs to the family of transition metal dichalcogenides crystallizing in the pyrite structure [1]. The semiconducting behaviour of this diamagnetic compound was verified by Hulliger on a polycrystalline sample [2]. In recent electrochemical investigations, RuS₂ has been attractive due to its effectiveness in petroleum refining as a catalyst for the thermal catalytic processing of organic sulphur and nitrogen compounds [3, 4], in electrolytic systems for the production of hydrogen [5], and in photoelectrochemical conversion of solar energy [6, 7]. Despite its technological importance, there are disagreements among several investigators concerning the fundamental properties of RuS₂. For example, there has been considerable controversy as to the value of the energy gap E_g for RuS₂, as reported in the literature. The values reported are 1.8 eV by Hulliger [2], 1.85 eV by Ezzaouia *et al* [7], 1.3–1.5 eV by Guittard *et al* [8], 1.5 eV by Redon [9], and 1.3 eV by Piazza *et al* [10] and Kuhne and Tributsch [11]. RuS₂ optical absorption studies were carried out by Bichsel *et al* [12] and Vaterlaus *et al* [13]; an energy gap of 1.3 eV and 1.22 eV at room temperature was reported, respectively. However, no detailed analysis of the absorption edges or their temperature dependence was reported.

In this paper we report the first detailed temperature-dependent optical absorption study of RuS₂ over a temperature range from 4.2 K to 300 K. An analysis of the absorption curve suggests that the interband transitions in RuS₂ are indirect. The energy gap E_g at various temperatures is determined and its temperature dependence is analysed by the Varshni equation [14] and an empirical expression proposed by O'Donnell and Chen [15]. The parameters that describe the temperature dependence of E_g are evaluated and discussed. At lower temperatures, several additional peaks superposed on the absorption curve are observed. The origin of these peaks will be discussed in the later sections.

2. Experimental details

Single crystals of RuS₂ were grown in tellurium fluxed [16]. Prior to the crystal growth a powdered compound was prepared from the elements (Ru 99.95% and S 99.999%) by reaction at 1070 °C for 10 days in an evacuated quartz ampoule. To improve the stoichiometry, sulphur with 2 mol% in excess was added with respect to the stoichiometric mixture of the constituent elements. The mixture was slowly heated to 1070 °C. This slow heating is necessary to avoid any explosions due to the strongly exothermic reaction between the elements. The powders so obtained were verified by x-ray diffraction to be in the pyrite structure. About 5 g of the starting material and 100 g of tellurium were sealed in an evacuated quartz ampoule. The ampoule was then brought to 1000 °C over a 24 h period and held at this temperature for 3 days. It was then cooled slowly at 1 °C h⁻¹ or 0.7 °C h⁻¹ to 700 °C, then cooled to room temperature in 24 h. The crystals were separated from the flux by dissolving the tellurium in aqua regia, with no apparent attack on the crystals. The crystals were then rinsed and cleansed in ultrasonic baths of deionized water and acetone. Single crystals of up to 7 × 6 × 5 mm³ were obtained.

Electrical resistivity and Hall effect measurements showed n-type semiconducting behaviour of the obtained single crystals. At room temperature, the carrier concentration is $1 - 4 \times 10^{18} \text{ cm}^{-3}$ and the Hall mobility is 200–300 cm² V⁻¹ s⁻¹. A paramagnetic species of spin $\frac{1}{2}$ was observed by electron paramagnetic resonance (EPR) in the crystals [16]. A sulphur point defect model is established to account for the paramagnetic species. This model assumes that an S²-S vacancy pair behaves like an electron donor. The electron probe microanalysis (EPMA) studies of the crystals indicated the sulphur deficiency of the crystals. Only a small amount of tellurium was detected and the average concentration of tellurium in the sample crystals varied from crystal to crystal. An inhomogeneous distribution of tellurium with locally higher concentration of tellurium was observed and ascribed to the peritectic reaction.

Measurements of the reflectivity and transmission at near-normal incidence were made on a Bruker model IFS 120HR. The instrumental resolution is 4 cm⁻¹. The reflectivity studies were done on the as-grown surface and compared against an evaporated gold mirror. For transmission measurements, the samples were cut into thin slices with a diamond saw parallel to the prominent face, (100). The faces were ground with successively finer grades of silicon carbide grinding paper to the final thickness of about 100 μm. The thickness and uniformity of the samples were measured with a micrometer with 10 μm resolution. The measurements were made at several temperatures between 4.2 K and 300 K with a temperature stability of 0.5 K or better. The specimens were mounted on a copper sample holder that fitted into a Dewar with optical windows. The temperatures were controlled with a heater wound near the sample and by controlling the flow of evaporating cryogenic fluids (helium or nitrogen).

3. Results and discussion

The transmission of the thin RuS₂ crystal was measured at near-normal incidence. The absorption coefficient α was determined from the transmission T_r by taking into account the spectral dependence of the reflectivity R using the relation [17]

$$T_r = \frac{(1 - R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}}. \quad (1)$$

Equation (1) assumes that there are multiple reflections within the sample, but that they add incoherently due to sample inhomogeneity or a sufficiently large spread of angles of incidence. Since αd is large for the sample crystals, the second term in the denominator of equation (1) can be neglected.

The major objective of this study is to determine the nature, the magnitude, and the temperature dependence of the energy gap E_g for RuS₂. To accomplish the task, a detailed analysis of the shape of the absorption edge needs to be carried out. In general, the absorption coefficient α is proportional to $(h\nu - E_0)^n$, where $n = \frac{1}{2}$ for direct transitions, $n = \frac{3}{2}$ for direct forbidden transitions, $n = 2$ for indirect transitions, and $n = 3$ for indirect forbidden transitions. E_0 is closely related to the energy gap. The indirect transitions involve the absorption or emission of a phonon in order to conserve momentum. Thus, in indirect transitions, the top of the valence band and the bottom of the conduction band occur at different wavevectors in the Brillouin zone. Figure 1 shows the absorption coefficient as a function of photon energy for a sample of 90 μm at several temperatures between 4.2 K and 300 K. As generally expected, the absorption edge shifts to higher energies as the temperature of the sample is lowered. At lower temperatures, several additional features are superposed on the absorption curves. From figure 1, analysis of the data (α against $(h\nu - E_0)^n$), $n = 2$ gives a better fit if the tail on the absorption edge at the lower value of α is disregarded. This suggests an indirect allowed transition. A more complete analysis of the data, taking into account both the absorption and emission of phonons, will be given as follows.

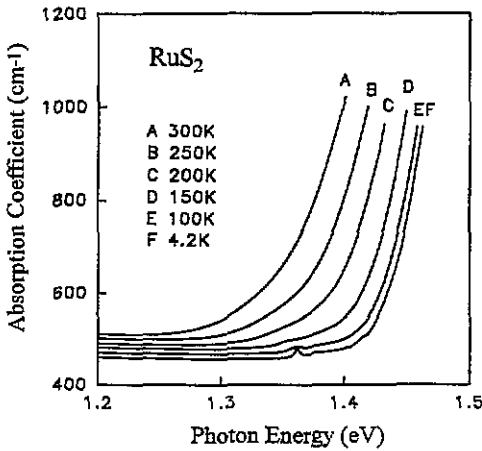


Figure 1. Absorption coefficient against photon energy for an RuS₂ single crystal at several temperatures between 4.2 K and 300 K.

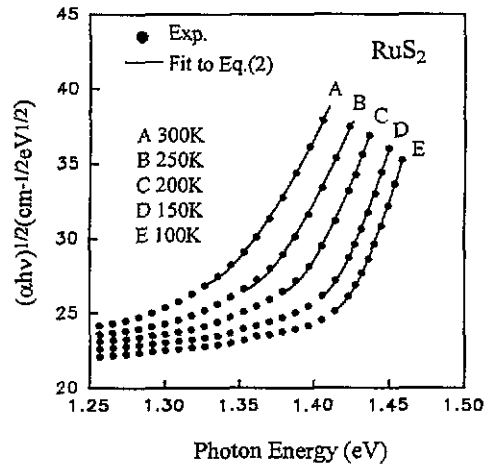


Figure 2. $(\alpha h\nu)^{1/2}$ against $h\nu$ for an RuS₂ single crystal at several representative temperatures. The solid circles are representative experimental points and the solid lines are the least-squares fits to equation (2).

For indirect allowed transitions, the absorption coefficient α for a single phonon process can be expressed as

$$\alpha(h\nu) = \frac{A(h\nu - E_g + E_p)^2}{\exp(E_p/k_B T) - 1} + \frac{B(h\nu - E_g - E_p)^2}{1 - \exp(E_p/k_B T)} \quad (2)$$

where $h\nu$ is the energy of the incident phonon, E_p is the energy of the phonon, E_g is the band gap, T is the absolute temperature, k_B is the Boltzmann constant, and A and B are constants [17]. The first term in equation (2) corresponds to absorption of a photon and a phonon, whereas the second term corresponds to absorption of a photon and emission of a phonon and contributes only for $h\nu > E_g + E_p$. The data at temperatures higher than 100 K are fitted to equation (2) and results are shown in figure 2, where the solid lines are the fits to equation (2). The fits are quite good. This makes us believe that RuS₂ is an indirect band gap semiconductor, in which a single phonon makes important contributions in assisting indirect transitions. Different values of E_g and E_p could be obtained by fitting a different energy range, i.e. by rejecting some points at lower or higher photon energies. An error of about 0.03 eV might be assigned to E_g . Fitting data on different samples gave similar parameters, even though there were differences in the absorption spectrum due to differences in sample thickness. The energy gap E_g at room temperature is determined to be 1.33 ± 0.3 eV. As shown in figure 1, at temperatures lower than 100 K several peaks are superimposed on the absorption curves. The existence of these features cause the difficulty of determining the band gap of RuS₂ by fitting the absorption data to equation (2). Therefore we propose that the energy gap of RuS₂ at low temperatures may be determined by adding the thermal ionization energy of the shallow donor states to the photoionization energy between the top of the valence band and these states. From analysing the temperature dependence of the spectral distribution of the absorption feature just below the band edge, the thermal ionization energy of these states may be estimated to be about 30 ± 10 meV. The energy gap below 80 K is determined to be 1.45 ± 0.02 eV.

The value of the band gap of RuS₂ has been the subject of much controversy in recent years. Originally a figure of 1.8 eV was accepted, based on diffuse optical reflection measurements on powdered samples [2]. From optical absorption measurements, assuming a constant reflection coefficient, Bichsel *et al* [12] estimated the energy gap of an RuS₂ single crystal at 1.3 eV. By taking into account the spectral dependence of the reflectivity, the energy gap was determined at 1.22 eV by Vaterlaus *et al* [13]. Attempts to determine the energy gap using a photoresponse spectra at semiconductor–electrolyte interfaces were also inconclusive. Guittard *et al* [8] first observed such a photoresponse spectrum using sintered RuS₂ electrodes, and suggested a value of 1.3–1.5 eV. However, in later work from the same laboratory, on single-crystal electrodes, the value obtained was 1.85 eV [7]. Nonetheless, in published spectra [18], a significant response to photons of energy below 1.8 eV is remarkably persistent at single-crystal surfaces. An even stronger photoresponse at the red end of the spectrum was observed using sintered electrodes and was interpreted in terms of donor levels close to the Fermi level and associated with structural defects in the material. However, the effect could also be interpreted in terms of an indirect energy gap or around 1.4 eV with a low transition cross-section, followed by a higher gap of 1.8 eV. Our results indicate that the lower end value is correct.

Holzwarth *et al* [19] reported the band structure calculation of RuS₂. The results show a completely filled Ru 4d t_{2g} band on top of the valence band and the bottom of the conduction band is formed by the S 3p σ^* antibonding states. The energy band dispersions of RuS₂ indicates that RuS₂ is an indirect gap semiconductor. The calculated indirect gap is 0.84 eV, due to the top of the valence band at X and the bottom of the conduction band at Γ . The value of 0.84 eV is much smaller than that obtained by our optical absorption measurements. The fact that the calculated gap is smaller than the experimental one is a general problem associated with using local density theory for studying semiconductors and insulators. The problem stems partly from the form of the exchange–correlation approximation [20] and

partly from the fact that the calculation is based on a ground-state theory and cannot be used rigorously to study excited-state properties such as optical spectra [21, 22].

Folkerts *et al* [23] reported the bremsstrahlung isochromat spectra of FeS₂, NiS₂, NiS_{1.2}Se_{0.8}, and NiSe₂, which is the first direct experimental evidence for a sharp antibonding p-like state above the Fermi level in these 3d transition metal pyrites. By adopting these results [18, 23], we therefore assign the indirect gap as the transitions between the Ru 4d *t_{2g}* and S 3p σ^* states. There is additional evidence to support our assignment. In the study of the photoelectrochemical evolution of oxygen with the RuS₂ electrode, we have observed that the RuS₂ crystal shows clear evidence of corrosion after photochemical oxidation by white light in 1 N H₂SO₄ for 10 h [24]. This result can be related to the fact that the excitations are from the Ru 4d *t_{2g}* to the S 3p σ^* antibonding molecular orbital, which tends to weaken the S–S bond in the pyrite structure.

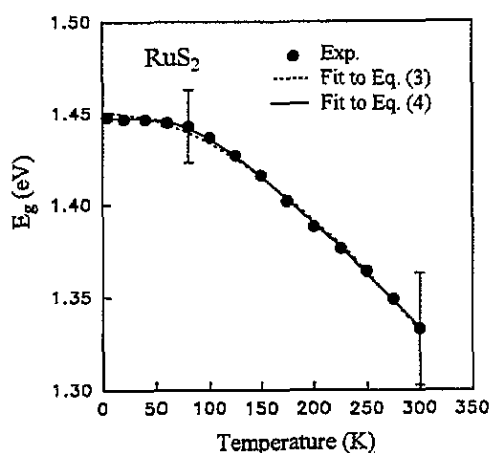


Figure 3. The temperature dependence of E_g of RuS₂. Representative error bars are shown. The dashed line is a least-squares fit to the Varshni equation [14]. The solid line is a least-squares fit to an empirical expression given by equation (4) proposed by O'Donnell and Chen [15].

Plotted in figure 3 are the temperature variations of the energy gap E_g . Representative error bars are shown. A least-squares fit (the dashed line) to the Varshni semiempirical relationship [14]

$$E_g(T) = E_g(0) - aT^2/(T + b) \quad (3)$$

yields the following parameters: $a = 1.2 \pm 0.2$ meV/K, $b = 621 \pm 40$ K, and $E_g(0) = 1.45 \pm 0.01$ eV, where $E_g(0)$ is the band gap at absolute zero, a and b are constants. a is related to the electron–phonon interaction and b is supposed to be related to the Debye temperature. The fit is rather poor at low temperature. Equation (3) predicts a quadratic temperature dependence of the energy gap at low temperature, whereas our experimental results indicate that the energy gap is almost temperature independent at low temperatures.

The data have also been fitted (solid line) to an empirical expression proposed recently by O'Donnell and Chen [15],

$$E_g(T) = E_g(0) - S\langle h\Omega \rangle [\coth(\langle h\Omega \rangle / 2k_B T) - 1] \quad (4)$$

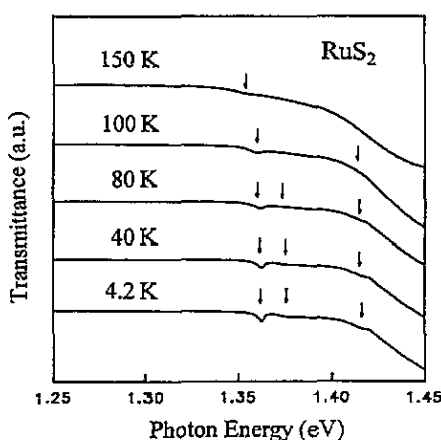


Figure 4. The transmittance spectra for an RuS₂ crystal grown in tellurium fluxes at 4.2, 40, 80, 100, and 150 K, respectively. The energy positions of various features are indicated by arrows.

where $E_g(0)$ is the band gap at zero temperature, S is a dimensionless coupling constant, and $\langle \hbar\Omega \rangle$ is an average phonon energy. The obtained values of $E_g(0)$, S and $\langle \hbar\Omega \rangle$ are 1.448 eV, 3.53, and 27.3 meV, respectively. The results show that equation (4) is compatible with reasonable assumptions about the influence of phonons on the bandgap energy of the material. Equation (4) gives a vastly improved fit of experimental data over the Varshni equation. Further, the parameters of the fit may be related to an intrinsic interaction of semiconductors, namely the electron-phonon coupling.

Now we examine the extra peaks of the sample at low temperatures. Figure 4 shows the transmittance spectra for a sample of RuS₂ grown in tellurium fluxes at 4.2, 40, 80, 100, and 150 K, respectively. At lower temperatures, the least three features are observed on the low-energy side of the transmittance spectra. These features shift to lower energies and become less pronounced when the temperature of the sample is higher than 100 K. At temperatures below 80 K, the positions of these features remain unchanged. Table 1 gives the position of these features at different temperatures.

Table 1. Energy positions of the impurity and defect-related features for RuS₂ single crystals grown in tellurium fluxed at different temperatures.

T (K)	E_1 (meV)	E_2 (meV)	E_3 (meV)
4.2	1363 ± 5	1376 ± 10	1417 ± 8
20	1363 ± 5	1376 ± 10	1417 ± 8
40	1363 ± 5	1376 ± 10	1417 ± 8
60	1362 ± 5	1375 ± 15	1416 ± 8
80	1361 ± 5	1373 ± 15	1415 ± 10
100	1360 ± 5	—	1413 ± 10
125	1357 ± 8	—	—
150	1353 ± 10	—	—

In order to identify the origin of the features shown in figure 4, a comparison with the EPR, EPMA, and electrical transport studies on the samples from the same batches is made. Electrical resistivity and Hall effect measurements showed an n-type semiconducting behaviour of the sample crystals. A single isotropic line was observed by EPR in RuS₂ crystals at temperatures below about 200 K [16]. The observed line is asymmetrical and can be fitted by a Dysonian lineshape [25]. A sulphur point defect is established to account for the spin $S = \frac{1}{2}$ paramagnetic species. The model assumes that an S²⁻-S vacancy pair behaves like an electron donor. The g -factor anisotropy is dependent on the degree of sulphur deficiency which is interpreted as due to the formation of a narrow band by the magnetic electrons of the sulphur defect below the bottom of the conduction band. According to the results of the EPR study, we may assign the origin of the feature located just below the band edge as the photoionization transitions between the top of the valence band and the S²⁻-S vacancy donor states, where the S²⁻-S vacancies form the shallow donor states. The first two features are related to the presence of tellurium in the RuS₂ crystals, since these two features were observed only on the samples grown in tellurium fluxes [26]. The results of the EPMA study of the sample crystals indicate that there are always small amounts of tellurium contained in the crystals and the average concentration of tellurium in the crystals varies from sample to sample [16]. When tellurium incorporated into RuS₂, it might act as an electron donor or form deep-level isoelectronic states. The fact that the electrical properties are not directly dependent upon tellurium concentration in the crystals reveals that tellurium is not a donor. Therefore the origin of these two features

is tentatively assigned as the photoionization between the deep-level tellurium isoelectronic states and the bottom of the conduction band. More systematic work is needed to establish conclusively the role of impurities and defects in RuS₂.

4. Summary

The optical absorption study of RuS₂ single crystals grown in tellurium fluxes is carried out over a temperature range from 4.2 K and 300 K. An analysis of the absorption curve shows that RuS₂ is an indirect band gap semiconductor. The temperature dependence of the band gap is analysed. The fitting of an expression proposed by O'Donnell and Chen improves over the semiempirical Varshni equation and gives information about the influence of phonons on the band gap of RuS₂. At temperatures lower than 100 K, three features occurring below the absorption edge are superposed on the absorption curve. The origin of these features is discussed. More systematic work is needed to establish conclusively the role of impurities and defects in RuS₂.

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