EPR Investigation of Synthetic, Doped FeS₂ and RuS₂ Single Crystals.

M. Schüler, J. Dahlem, and D. Siebert

Institut für Physikalische Chemie, Albert-Ludwigs-Universität, Albertstr. 23a, 79104 Freiburg i. Br.

Z. Naturforsch. 50 a, 1159–1164 (1995); received October 17, 1995

Synthetic FeS₂ and RuS₂ single crystals were prepared by the flux method using PbCl₂, bismut, and tellurium as different solvents. FeS₂ and some RuS₂ samples were doped with elementary vanadium, other RuS₂ crystals with manganese and nickel. The EPR spectra revealed Mn²⁺ in the low-spin state and Ni²⁺. The lineshape of the Mn sextet turned out to be asymmetrical. In some RuS₂ samples we detected an isotropic structureless rather narrow signal with a linewidth down to 0.05 mT and attributed it to the conductivity. Its lineshape becomes symmetrical and Lorentzian by grinding the samples to a polycrystalline powder. The EPR parameters of appropriate spin-Hamiltonians were determined. The intensities of the allowed and forbidden lines depended very differently on the microwave power due to different degrees of saturation.

Key words: FeS₂, RuS₂, EPR, paramagnetic ions, conductivity.

1. Introduction

RuS₂ and FeS₂ belong to the family of transition-metal dichalcogenides crystallizing in the pyrite structure. There is an increasing interest in synthetic pyrite (cubic FeS₂) with regard to its electrical conductivity and photovoltaic properties [1]. In electrochemical investigations the ruthenium compounds have been attractive as electrode or photoelectrode materials because of their catalytic properties [2] and favourable stability [3].

Formerly we detected and investigated several paramagnetic species in single crystals of FeS₂ [4, 5, 6] and in RuS₂ [7]. Yu et al. performed similar EPR measurements with FeS₂ [8] that agree with ours essentially.

Furthermore they studied paramagnetic species of electronic spin S = 1/2 in undoped, as-grown RuS₂ single crystals [9] and in solid solutions Ru(S₁₋ₓSeₓ)₂ [10]. They reported on Mn²⁺ in the low spin state in RuS₂ [11], determined a g₉ of 2.135 and a hyperfine constant of 0.0081 cm⁻¹. Tsay et al. [12] prepared single crystals of Ru₃Fe₁₋ₓS₂ by chemical vapour transport and flux methods and proposed S⁻ associated with an S vacancy. In this paper we report on an EPR study of several new, paramagnetic centers in FeS₂ and RuS₂, produced by extra doping.

2. The Crystals

2.1. FeS₂

V-doped crystals were obtained from a PbCl₂ melt. We prepared mixtures of FeS₂ powder and PbCl₂ 99.999 % in a ratio of 1:12 by weight together with 10 mol% vanadium powder in evacuated and sealed quartz ampoules. These ampoules were heated to 850 °C and then slowly cooled at a rate of 2 °C/h down to 500 °C. To separate the FeS₂ crystals from the solid melt, PbCl₂ was dissolved in 16 % HCl and 2M NaOH. Single crystals up to 4 mm edge length could be obtained.

2.2. RuS₂

The crystals doped with elementary vanadium (10 mol%) or nickel (10 mol%) were grown from solutions with bismut as a solvent [13], and the Mn-doped crystals were obtained from a Te melt [14]. We prepared mixtures of RuS₂ powder and bismut (99.999 %) in a ratio of 1:40 by weight, and for the Mn-doped crystals mixtures of RuS₂ powder and tellurium in a ratio of 1:32 by weight together with 10 mol% manganese powder in evacuated and sealed quartz ampoules. These ampoules were heated to 1040 °C and then slowly cooled at a rate of 2 °C/h down to 500 °C and at a rate of 1 °C/h down to 550 °C,

Reprint requests to Prof. Dr. D. Siebert.

0932-0784 / 95 / 1200-1159 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72072 Tübingen
respectively. To separate the RuS₂ crystals from the solid melt, bismut was dissolved in 30 % HN0₃, and the solid tellurium melt in aqua regia. Single crystals up to 4 mm edge length could be obtained.

3. EPR Spectra and Analysis

3.1. Experimental

Our EPR measurements were performed at 78 K with a conventional Varian X-band spectrometer and a standard TE₁₀₂-cavity with 100 kc modulation. At room temperature the cavity loading was too high for the crystal used, because of their conductivity. The X-band frequency was measured with a frequency counter, the magnetic field by a Bruker NMR magnetometer. The crystal structure of FeS₂ and RuS₂ is the well known pyrite structure. The space group is P2₁/a₃, the cation sites and the sites of the S₂ dumb-bells have the local symmetry 3. For those investigated centers that were orientational dependent, we observed four lines for each transition. This site splitting agreed with the local symmetry 3, the 3 axes being parallel to the four different (111) directions. In consequence the signals were attributed to substitutional centers.

It was convenient to use the site splitting for an accurate setting of the crystal orientation, especially for \( \mathbf{B}(\theta) \parallel \{100\}, \{110\} \) and \( \{111\} \), where signals coincide. For \( \Theta \), the angle between center axis and magnetic field, we realized the values 54.7°, 35.3° and 90.0°, 0.0° and 70.5°, respectively [4]. Furthermore we studied the EPR lines qualitatively at different microwave powers to get some information about the saturation behaviour of the centers.

3.2. Analysis of the Spectra

The EPR parameters were obtained from the spectra by a computer fitting procedure [4]. This program compared experimental and calculated magnetic fields for an assumed set of EPR parameters. The resonance fields were calculated by means of exact numerical diagonalization of the spin-Hamiltonian matrices. For each transition the quantum mechanical transition probability

\[ |\mu_{ij}|^2 \propto |< i | \mathcal{H}_1 / \beta B_1 | j >|^2 \]

was calculated from the diagonalization procedure. \( \mathcal{H}_1 \) denotes the Zeeman operator due to the magnetic field \( B_1 \) of the microwave [4].

3.3. V-doped Crystals

In both RuS₂ and FeS₂ we found a distinct hyperfine structure (HFS) corresponding to a nuclear spin \( I = 7/2 \) and several small lines within the HFS (Figure 1). The signal octet of the resonance varied from about 0.16 to 0.32 Tesla, characteristic for \( S = 3/2 \) in a strong axial field. Furthermore we were able to detect the signals expected at higher fields near 0.5 Tesla for \( B(\theta) \parallel \{111\} \) and 0.7 Tesla for \( B(\theta) \perp \{111\} \) (cf. Cr³⁺ in RuS₂, Fig. 3 in [7]).
Table 1. EPR parameters for RuS₂ and for FeS₂; cm⁻¹, \( A_{||}, A_{\perp}, A_0, T \) in 10⁻⁴ cm⁻¹; *: parameters are determined in this work.

|          | \( g_{||} \) | \( g_\perp \) | \( b_2^0 \) | \( A_{||} \) | \( A_{\perp} \) | \( A_0 \) | \( T_{||} \) | Ref. |
|----------|------------|-------------|-----------|-------------|-------------|------|----------|------|
| RuS₂     |            |             |           |             |             |      |          |      |
| V²⁺      | 2.0040     | 2.0000      | 0.407     | 47.9        | 52.6        | —    | —        | *    |
| Mn²⁺     | 2.0185     | 2.1435      | —         | —           | —           | —    | —        | —    |
| Ni²⁺     | 2.1053     | 2.1122      | (-)       | 1.729       | —           | —    | —        | —    |

| FeS₂     |            |             |           |             |             |      |          |      |
| V²⁺      | 2.0101     | 2.0035      | 0.3601    | 44.1        | 48.3        | —    | —        | *    |
| Mn²⁺     | 2.0377     | 2.1490      | —         | 8.7         | 75.1        | 47.2 | -55.9    | [4]  |
| Ni²⁺     | 2.0921     | 2.0893      | (-)       | 15.5        | 13.0        | —    | —        | [5]  |

The received data can be described satisfactorily with the specialized spin-Hamiltonian for electronic spin \( S = \frac{3}{2} \) and the above nuclear spin [5]:

\[
\mathcal{H} = g_{||} \beta B_z S_z + \left( \frac{1}{2} \right) g_\perp \beta \left( B_x S_- + B_- S_+ \right) + \frac{b_2^0}{3} (3S_z^2 - S(S + 1)) + A_{||} S_z I_z + \left( \frac{1}{2} \right) A_{\perp} (S_+ I_- + S_- I_+). \tag{3}
\]

The strong lines in Fig. 1 represent the allowed transitions with \( \Delta m = 0 \) and the small lines the forbidden transitions with \( \Delta m = 1 \). The EPR spectrum of V-doped FeS₂ is shown in Fig. 1 for \( \Theta = 54.7° \). The stick diagram shows an excellent agreement of the experimental and theoretical spectrum. This is representative also for the other characteristic angles. The EPR parameters are listed in Table 1. The hyperfine parameters \( A_{||} \) and \( A_{\perp} \) were determined from the resonances \( B_0 || z \) and \( B_0 \perp z \), correspondingly.

3.4. Mn-doped Crystals

The EPR spectrum is presented in Fig. 2 for \( B_0 || (111) \). There is a sextet for \( \theta = 0° \) and another one for \( \theta = 70.5° \) with threefold intensity. As in similar investigations on FeS₂ [4] we analyzed the spectrum by the specialized spin-Hamiltonian for an electron spin \( S = \frac{1}{2} \) and nuclear spin \( I = \frac{5}{2} \) of the \( ^{55} \text{Mn} \) nucleus for axial symmetry:

\[
\mathcal{H} = g_{||} \beta B_z S_z + \left( \frac{1}{2} \right) g_\perp \beta \left( B_x S_- + B_- S_+ \right) + A_{||} S_z I_z + \left( \frac{1}{2} \right) A_{\perp} (S_+ I_- + S_- I_+). \tag{4}
\]

The good agreement of the calculated fields at resonance with the experimental values in Fig. 3 proves, that Mn²⁺ is in the low-spin state in RuS₂ as in FeS₂.
Furthermore we observed an asymmetric lineshape of the signals.

### 3.5. Ni-doped Crystals

In Ni-doped RuS₂ we found an EPR signal without HFS which varied between 0.19 and 0.79 mT, and its intensity decreased from higher to lower magnetic fields. This is characteristic for a transition that becomes forbidden between the pure states |−1⟩ and |1⟩, i.e. the spin has to be integer. The observation is similar to that of Ni²⁺ in FeS₂ [5]. Therefore we analyzed the different resonance lines with the spin-Hamiltonian (see (3)) for electronic spin \( S = 1 \) and nuclear spin \( I = 0 \) and found a very good agreement with the experimental values as shown in Figure 4. The determined EPR-parameters are listed in Table 1.

![Fig. 4. Angular variation of Ni²⁺ in RuS₂; • • • experimental values; ---- • • • theoretical values; • • • small transition probability.](image)

4. Discussion

#### 4.1. FeS₂: V and RuS₂: V

Similar to previous investigations we found that the \( g \)-value for V²⁺ is greater than the free electron value, \( g_e \), although the shell of d-electrons is less than half-filled. We conclude that there is a strong covalent bond in FeS₂ and in RuS₂. But in RuS₂ the \( g \)-values are nearer to \( g_e \) and the values for \( A_{||} \) and \( A_{\perp} \) are greater than in FeS₂. According to this, the covalency of the sulfur bond in RuS₂ is smaller.

As V²⁺ and Cr³⁺ are isoelectronic with the configuration \((Ar)3d³\), we determined the following ratios (see Table 1):

\[
A_{||}(Cr³⁺)/A_{||}(V²⁺) = 0.284 \text{ for FeS₂},
\]

\[
A_{\perp}(Cr³⁺)/A_{\perp}(V²⁺) = 0.277 \text{ for FeS₂},
\]

\[
A_{\perp}(Cr³⁺)/A_{\perp}(V²⁺) = 0.277 \text{ for RuS₂},
\]

This has to be compared with \( |g_N|/(Cr³⁺)/|g_N|/(V²⁺) = 0.214. \) The result shows an approximate agreement between the ratios of HF constants and the ratios of the nuclear magnetic moments, i.e. the ratios of the
The dependence of the EPR signals from the microwave power originates from a well known saturation phenomenon described in [17, 18]. With increasing value of microwave power the intensities of the strong lines were quenched and the small lines grew stronger. The mechanism can be explained qualitatively with relation for the power absorbed by the spin system

$$\frac{dW}{dt} = \frac{\Delta N \hbar w_{ij}}{1 + 2w_{ij} \tau_1},$$

where \(\tau_1\) denotes the spin-lattice relaxation time, \(\Delta N = N_i - N_j\) the population difference between an upper level \(j\) and a lower level \(i\) of a simple two-level system in the equilibrium state. For the number of transitions between the energy levels, which are induced by an oscillatory field of amplitude \(B_1\) and angular frequency \(\omega\), is

$$w_{ij} = \frac{\pi B_1^2}{2\hbar^2} |\mu_{ij}| f(\omega).$$

For linear detectors the absorption signal detected experimentally is proportional to the out of phase magnetization component \(B_1\chi''\), and one obtains

$$B_1\chi'' = \frac{2\hbar|\mu_{ij}|^2 B_1 \Delta N C(\omega)}{1 + 2C(\omega)B_1^2|\mu_{ij}| \tau_1},$$

where \(C(\omega)\) describes the lineshape. Referring to (8) the strong lines with high transition probabilities \(|\mu_{ij}|\) can be saturated earlier than the weaker lines according to lower transition probabilities for the latters (see Figures 1a and b). This phenomenon had been found by us in RuS\(_2\) as well, but at higher microwave power because of additionally inhomogenous broadening effects.

4.2. RuS\(_2\): Mn

Compared with results from Mn-doped FeS\(_2\) crystals we assign the spectrum of Fig. 2 to Mn\(^{2+}\) in the low-spin state on a cation site in RuS\(_2\), as assumed for Ru\(^{3+}\). Yu et al. [11] reported a \(g_{||} < 0.5\) and a \(g_{\perp} = 2.135\) from a powder spectrum. Now we were able to find a whole angle variation and also it was possible to determine the complete set of EPR parameters (see Table 1). The value for \(A_{\perp} = 0.0081\) cm\(^{-1}\) of Yu et al. [11] is in agreement with our measurements.

Following [16] the hyperfine interaction tensor \(A\) is decomposed as usually in an isotropic part \(A_0\) with the principal value \(A_0\) and a traceless tensor \(T\) with principal values \(T_{\perp}\) and \(T_{||} = -2T_{\perp}\) (see Table 1). For \(T_{||}\) a simple one electron model predicts \(T_{||} = -\frac{2}{3}g\beta g_N\beta_N(r^3)\) [6, 15]. After the tables of atomic parameters [15] we get \(T_{||} = -160\) MHz and experimentally \(-175\) MHz corresponding to \(-0.00586\) cm\(^{-1}\). With regard to the crude approximation that does not consider the orbitals of the ligands, the agreement is quite good.

For the isotropic part \(A_0\) we obtained 0.00518 cm\(^{-1}\). As in FeS\(_2\) we explain this by a very small admixture of 4s states that is higher in RuS\(_2\) compared to FeS\(_2\). This may be due to the higher lattice constant [19, 20] and the 4s electrons could claim more room. According to Koh and Miller [15] a pure 4s electron centered on Mn\(^{2+}\) would produce an isotropic hyperfine constant of 4731 MHz compared to only 155.3 MHz from Table 1.

The asymmetry of the EPR signals is a consequence of the high conductivity of the crystals. If the skin depth is much smaller than the thickness of the crystals, the observed line is a mixture of a dispersion and an absorption curve [21].

4.3. RuS\(_2\): Ni

Because of doping RuS\(_2\) with elementary nickel and due to the spin value \(S = 1\) we assigned Ni\(^{2+}\) on Ru site to the observed EPR resonance. The result is similar to that of Ni\(^{2+}\) in FeS\(_2\) [5]. We were not able to measure the weak HFS of the isotope \(^{61}\text{Ni}\) with a nuclear spin \(I = 3/2\) because of the broadened lines due to interactions with the nearest Ru neighbours \((I = 5/2\) for \(^{99}\text{Ru}\) (12\%) and \(^{101}\text{Ru}\) (17\%)). The \(g\) values of Ni\(^{2+}\) in RuS\(_2\) are greater than the free electron value, as it should be for more than five d electrons. Compared with FeS\(_2\), they are smaller than usually as well, but nearer to the values (2.20-2.25) obtained in many oxides. The result indicates that the covalency of the sulfur bond in RuS\(_2\) is smaller than in FeS\(_2\), in accordance with previous discussions of Cr\(^{3+}\) [7] or V\(^{2+}\) in the above section.

4.4. Isotropic Resonance

The detection of an isotropic single EPR line is reported by Yu et al. [10]. They studied a paramagnetic center with an electronic spin \(S = 1/2\) and
found an anisotropic $g$-factor. After recrystallization from small crystals without adding an extra amount of sulfur to the starting material, the anisotropy of the $g$-factor was much reduced. This observation had been confirmed after heating of some crystals in sealed quartz ampoules at 1100°C for 5 days. Now the EPR spectrum consisted of an isotropic line with a $g$ value of 2.068 ± 0.001 which agrees with ours very well. But the line breadths between 0.89 and 1.7 mT of their signals were greater than that of our isotropic resonance with only 0.05 mT linewidth.

Yu et al. concluded that the isotropic line originates from delocalized electrons as arising from an overlap of the wave functions due to the sulfur deficiency. They assumed the formation of a narrow band within the gap of RuS$_2$ in agreement with Birkholz et al. [22]. The Lorentzian line shape, demonstrated by us in Fig. 5b, is characteristic for delocalized electrons. The conclusion is confirmed by the fact of high cavity loading at room temperature.

**Acknowledgements**

Financial support of the “Deutsche Forschungsgemeinschaft” and the “Fonds der Chemischen Industrie” is gratefully acknowledged.