Crystal structure and magnetic interactions in ZrCr$_2$S$_4$

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Abstract. The evaluation of exchange integral intensities J_i is extended to the fourth order ($i = 1, 2, 3, 4$) for the spinel sulphur. We have performed EPR and dilatation measurements on a single crystal in the temperature range 4.2 K $\leqslant T \leqslant 300$ K. The J_i-value is compared with that deduced from EPR measurements. Dilatation measurement confirms the absence of any tetragonal distortion as found by neutron diffraction.

A comparison between results obtained on a polycrystal and a single crystal is given.

1. Introduction

ZnCr$_2$S$_4$ is a normal spinel with a lattice parameter $a = 10.001$ Å and a sulphur position parameter $u = 0.3845$ obtained from the position of Bragg peaks and nuclear intensities measured on a pure polycrystal [1]. The variation in R-factor versus the sulphur parameter u allows one to estimate the accuracy as of the order of 0.003 [1].

In the paramagnetic region, Curie–Weiss behaviour has been observed above 100 K with $\Theta_p = 18$ K [2]. Below the Néel temperature $T_N = 15.5$ K, the chromium spin orders antiferromagnetically and the structure is helimagnetic. At $T_0 = 12$ K, other phases appear and persist until 0 K. For $T_0 \leqslant T \leqslant T_N$, only the incommensurable phase remains; T_0 agrees with a first-order transition [1].

The Mössbauer spectrum of the ZnCr$_2$S$_4$ polycrystal doped at 2% Fe at high temperatures ($T > T_N$) consists of a single line ($\epsilon = 0$) with an isomer shift $\delta = 0.80$ mm s^{-1} typical for Fe^{2+} in a tetrahedral environment [3]. This proves that only Zn^{2+} ions were substituted by Fe^{2+}.

At low temperatures, the coexistence of three magnetic phases, responsible for the reversibility of properties established for single-crystal magnetization, is confirmed and the values of the hyperfine parameters are given [3].

In the oxyspinel ZnCr$_2$O$_4$ and the selenospinel ZnCr$_2$Se$_4$, irreversibility effects have been observed at small fields [4,5] depending on the direction of the applied field. In these compounds, the irreversibility results from an increase in the size of favoured magnetic domains.

The weak Θ_p-value implies weak magnetic interactions and this positive value seems to be incompatible with the antiferromagnetism of ZnCr$_2$S$_4$. In order to obtain more information about the magnetic structure, it is necessary to determine exchange integral intensities between more distant neighbours J_i ($i > 1$). Our proposal is to calculate the J_i ($i = 1, 2, 3, 4$) on the basis of neutron and magnetic results [1,3], to derive the J_1-value from EPR measurements and to make a comparison between these results. We have performed

dilatation measurements on a single crystal in the temperature range 4.2 K $\leqslant T \leqslant$ 300 K. These measurements show the absence of stoichiometric effects.

2. Dilatation measurements

Measurements have been performed on a single-crystal $ZnCr_2S_4$ sample in the temperature range 4.2 K $\leqslant T \leqslant$ 300 K. In the limit of experimental errors the dilatation coefficient $\alpha_T = (1/a)(\partial a/\partial T)$ remains equal to zero for $T \leqslant 6$ K. For 6 K $\leqslant T \leqslant$ 12 K, α_T is positive and weak ($\alpha_T \leqslant 5 \times 10^{-6}$ K^{-1}). For 12 K $\leqslant T \leqslant$ 300 K, the α_T-values do not present any marked peak at T_N. So, no significant tetragonal distortion occurs as seen by neutron measurements.

3. EPR measurements

EPR measurements were performed on a single crystal in the temperature range 4.2 K $\leqslant T \leqslant$ 300 K. The spectrum always consists of a single symmetrical absorption line and its linewidth remains constant above $T = 150$ K. Therefore, $\Delta H_{pp}(T)$ (peak-to-peak linewidth in the first-derivative spectrum) at room temperature may be considered as $\Delta H_{pp}(\infty)$. At $T = 288$ K, the lineshape is Lorentzian with $g = 1.99$ and $\Delta H_{pp} = 150$ G (figure 1).
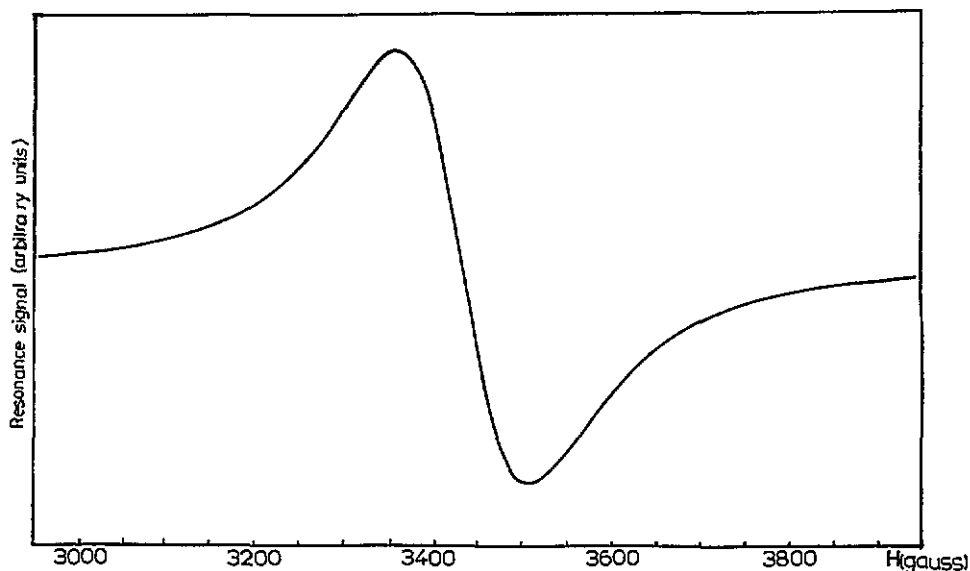

Figure 1. EPR spectrum (absorption derivative) for a single crystal of $ZnCr_2S_4$ at $T = 288$ K.

We first calculated ΔH_{pp} considering only dipolar broadening and neglecting exchange-narrowing effects. Van Vleck's [6] method is applied. The corresponding ΔH_{pp}(dip) is about 1500 G (only the six nearest neighbours are considered).

The line is Lorentzian with $\Delta H_{pp} = 150$ G suggesting a narrowing by exchange. Following the theory of Anderson and Weiss [7], the half-width at half-power for an

exchange narrowed is given by $\Delta\omega = \omega^2 d/\omega_e$, where ω_d is the dipolar linewidth and ω_e the exchange frequency. The value of ω_e is proportional to $\Delta H_{pp}(\text{dip})/\Delta H_{pp}$ [8] and related to J_1 by $\omega_e = 1.68(J_1/g\mu_B)[S(S+1)]^2$ (μ_B is the Bohr magneton). The J_1-value deduced is 1.75 K.

The model of calculation, even if valid only for the simple-cubic lattice, was shown to give good results for the spinel lattice also [9].
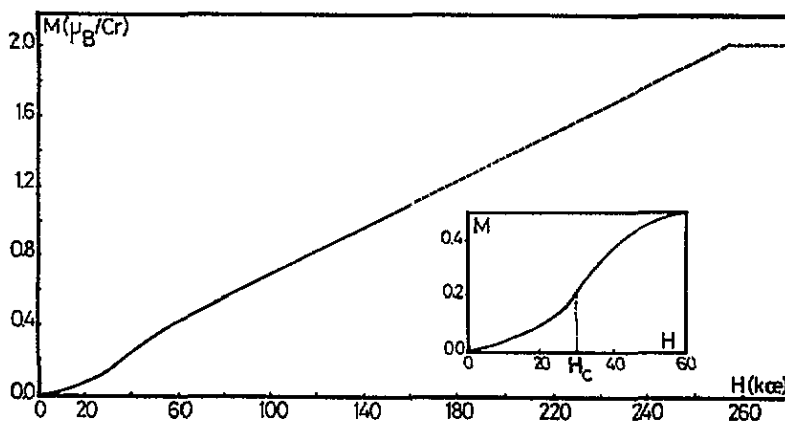

Figure 2. Schematic variation in the magnetization of a single crystal of ZnCr$_2$S$_4$ up to saturation at $T = 4.2$ K.

Table 1. Comparison between results obtained for a single crystal and a polycrystal.

(a)	μ_s (μ_B)	H_c (kOe)	Ref.					
Single crystal	2.00	30						
Polycrystal	2.56	$\geqslant$150	[11] [1]					

(b)	Ref.	J_1 (K)	J_2 (K)	J_3 (K)	J_4 (K)			
Single crystal		2.66	-1.15	0.29	0.13			
Polycrystal	[11]	1.87	-0.76	0.29	0.14			
	[1]	2.05	-1.00	0.95				

(c)	Ref.	J_{aa} (K)	J_{ab} (K)	J_{ac} (K)	λ_H (K)	λ_{M_1} (K)	λ_{M_2} (K)
Single crystal		7	1.96	-2.28	8.98	8.98	8.89
Polycrystal	[11]	5.46	1.96	-0.72	6.16	6.20	5.91
	[1]	7.90	-0.20	3.60	6.20	7.00	6.30

4. Evaluation of J_1, J_2, J_3 and J_4 using molecular-field theory

We have considered that the magnetic properties of the ZnCr$_2$S$_4$ system can be described by the classical Heisenberg Hamiltonian:

$$H = 2 \sum_{ij} J_{ij} S_i S_j. \tag{1}$$

$J_{ij}(k)$ are the elements of a matrix $\mathbf{J}(k)$ and represent the Fourier transform of the exchange integrals. Let $\lambda(k_0)$ be the highest eigenvalue of $\mathbf{J}(k_0)$ for a magnetic structure of wavevector k_0; the associated energy is given by $E(k_0) = -\lambda(k_0)S^2$. To calculate J_1, J_2, J_3 and J_4 we need four equations. The first is taken from the experimental value of the Curie–Weiss temperature:

$$\Theta_p = \tfrac{2}{3} S(S+1) \sum_{i=1}^{4} Z_i J_i \qquad (Z_i = 6, 12, 12, 12). \tag{2}$$

The second is given by the expression for the cosine of the helical angle Φ [10]:

$$\cos \Phi = \tfrac{1}{6} J_4 [-(J_2 + 2J_3) + \{(J_2 + 2J_3)2 - 3J_4(J_1 + 2J_2 - 2J_4)\}^{1/2}]. \tag{3}$$

The coexistence of the helimagnetic structure (indicated by subscript H) defined by the wavevector $k_1(0, 0, 0.79)$ and two modulated structures (indicated by subscripts M_1 and M_2) defined by the wavevectors $k_2(\tfrac{1}{2}, \tfrac{1}{2}, 0)$ and $k_3(0, 1, \tfrac{1}{2})$ suggests the equality of their free energies (λ_H, λ_{M_1} and λ_{M_2}). We can write $\lambda_H(k_1) = \lambda_{M_1}(k_2)$, so that we obtain

$$2J_1(1 + \cos \phi) + 4J_2[(2\cos \Phi + \cos 2\Phi)] + 4J_3[1 + 2\cos(2\Phi)] + 4J_4[1 + 2\cos \Phi \cos(2\Phi)]$$
$$= J_1 + 2J_2 - 2J_4 + [(J_1 - 2J_2 - 2J_4)^2 + 8J_1^2]^{1/2}. \tag{4}$$

At the critical field $H_c = 30$ kOe (figure 2), the helimagnetic structure is transformed into a conical structure typical of a ferromagnetic mode; so we obtain the fourth equation

$$\mu_s H_c = \lambda_F(0, 0, 0) - \lambda_H(0, 0, 0.79) \tag{5}$$

where μ_s is the saturation magnetization of the chromium spin and $\lambda_F(0, 0, 0)$ is the energy of the ferromagnetic structure ($\lambda_F(0, 0, 0) = \sum_{i=1}^{4} Z_i J_i$).

Using equations (2)–(5), we can determine the fourth-nearest-neighbour interactions and the classical energies of different structures. The optimum values are given in table 1(a)–(c). We have also presented the couplings between planes. For in-plane coupling, $J_{aa} = 2J_1 + 4J_3 + 4J_4$. For inter-plane coupling, $J_{ab} = 4J_1 + 8J_2 + 4J_4$. For coupling between second-nearest neighbours, $J_{ac} = 4J_2 + 8J_3$.

5. Discussion

The value of J_1 obtained at low temperatures ($J_1 = 2.66$ K) is slightly superior to that obtained by EPR ($J_1 = 1.75$ K) in the paramagnetic region. This difference could be the effect of temperature on the Cr–Cr binding, and therefore on the Cr–S–S–Cr superexchange.

The couplings between planes are in agreement with helimagnetic order ($J_{aa} > 0$, $J_{ab} > 0$ and $J_{ac} < 0$).

According to the Goodenough–Kanamori [12, 13] rules, a positive sign was predicted for J_1 and J_4 and a negative sign for J_2, J_3 and J_5.

The application to $ZnCr_2S_4$, which is presented in table 1(b), yields an antiferromagnetic interaction between second-nearest neighbours and a ferromagnetic coupling for the first-,

third- and fourth-nearest neighbours. J_3 is considered as an average of direct and masked couplings.

The magnetization value of chromium obtained in the single-crystal form ($\mu_s = 2\mu_B$) is much weaker than obtained in the polycrystal ($\mu_s = 2.56\mu_B$). These two values are lower than the theoretical value ($\mu_s = 3\mu_B$). The unsaturated value of the Cr moment results from the existence of magnetic domains at low temperatures [14]. The inflection point at $H_c = 30$ kOe on the magnetization curve may be considered as an average initial field corresponding to a spin-flop transition for the collinear structures and a transition to a fan structure for the helical structure. The schematic variation in the magnetization up to saturation presented in figure 2 suggests a higher-field saturation value. More discussion has been given in [3, 15].

Acknowledgments

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