

EPR STUDY OF THE PARAMAGNETIC Cr^{+3} ION IN COMPOUNDS OF SOME METAL (I) CHROMIUM (III) SULFIDES AND SELENIDES

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Electron paramagnetic resonance measurements were performed for paramagnetic Cr^{+3} ions in $A\text{CrX}_2$ -type compounds, where A represents Na, Ag or Li and X represents S or Se. The purpose of the experiments was to calculate the electronic g -factors, the effective magnetic moments $\vec{\mu}_{\text{eff}}$ and the dipolar shifts of the EPR lines. Line shapes and widths were also determined.

1. Introduction

Details of the ESR spectrum analysis for $A\text{CrX}_2$ -type powders (where A represents Na, Ag or Li and X represents S or Se) are presented in this paper. The values of the electronic g -factor, the effective magnetic moment $\vec{\mu}_{\text{eff}}$ and the g -shift are calculated (see Section 3). The line shape is also described. Section 2 is a review of the magneto-optical features of $A\text{CrX}_2$ -type compounds and of recent experiments performed on these samples.

2. Structural and magneto-optical features of $A\text{CrX}_2$ -type compounds

Compounds of the type $A\text{CrX}_2$ are antiferromagnetic layers having low Neel temperatures (see Table I). Their magnetic and crystallographic structures have been determined by neutron diffraction [1-3]. The NaCrS_2 and NaCrSe_2 crystals belong to the space group $R\bar{3}m(D_{3d}^5)$, AgCrS_2 and AgCrSe_2 — to the space group $R3m(C_{3v}^5)$. The Cr^{+3} ions occupy octahedral holes so that CrX_2^- sandwiches are formed. Between these sandwiches, monovalent cations are situated, Na^+ in octahedral holes, Ag^+ in half of the tetrahedral holes (Fig. 1a, b). The structure of the LiCrS_2 compound has been described in [3]. This structure has two possibilities: (a) a space group $P\bar{3}(C_{3i}^1)$ and (b) $P3(C_3^1)$. In the first case the Li atoms are located in octahedral holes, and in the second they occupy tetrahedral holes. The results

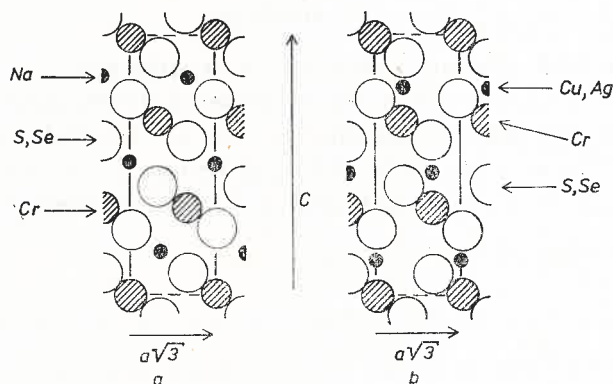
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TABLE I

Magnetic properties of the $ACrX_2$ compounds ($A = Na, Ag, Li, X = S, Se$)

	NaCrS ₂	NaCrSe ₂	AgCrS ₂	AgCrSe ₂	LiCrS ₂
Asymptotic Curie temperature θ (K)	+30	+108	-55	+72	-276
Neel temperature T_N (K)	19	40	40	50	55
the molar Curie constant C_M	1.79	1.84	1.71	1.70	1.84
the deduced number of unpaired electrons q	2.91	2.96	2.83	2.82	2.96
the moments of the Cr^{+3} ions μ_{Cr} (μ_B)	2.48(4)	2.63(3)	2.60(3)	2.55(3)	2.26
paramagnetic effective moments μ_{eff} (μ_B)	3.78	3.84	3.70	3.69	3.837

of X-ray diffraction have shown that in LiCrS₂ both the Cr and Li ions are located in the octahedral holes of the hexagonal close packed array of sulphur atoms. The magnetic structures of these compounds are shown in Fig. 2. The magnetic properties of these compounds are presented in [1-3] and in Table I. We see that the NaCrS₂, NaCrSe₂ and AgCrSe₂ crystals have positive paramagnetic Curie temperatures. This suggests that the dominating intralayer interaction between the Cr^{+3} ions is positive or that their magnetic

Fig. 1. Section through the $(11\bar{2}0)$ plane of: (a) NaCrS₂(Se₂), (b) CuCrS₂(Se₂) and AgCrS₂(Se₂)

structure below the Neel temperatures consists of ferromagnetic layers that are antiferromagnetically coupled. The paramagnetic Curie temperatures θ of AgCrS₂ and LiCrS₂ are negative and so ferromagnetic layers of Cr^{+3} ions are not present below T_N . From above T_N up to about 2θ , AgCrSe₂, NaCrSe₂ and NaCrS₂ crystals show large deviations from the Curie-Weiss law of susceptibility. This indicates a large amount of short-range magnetic order within the layers. The magnetic susceptibility of AgCrS₂ and LiCrS₂ follows the Curie-Weiss law. In [3] it is shown that the LiCrS₂ susceptibility is slightly field dependent below 200 K.

Table I lists the values of the molar Curie constant C_M , the observed magnetic moment of Cr^{+3} ions $\vec{\mu}_{\text{Cr}}$, the paramagnetic effective moment $\vec{\mu}_{\text{eff}} = \sqrt{8C_M}$ that corresponds to the number of unpaired electrons q . We see that the values of C_M for our samples are close to the spin only value of 1.87 for pure spin $S = 3/2$ expected for Cr^{+3} ions and that the μ_{Cr} 's for all $A\text{CrX}_2$ type crystals are much smaller than the expected value of $3\mu_B$. This last item suggests evidence of covalency effects on the distribution of magnetic moments around the Cr^{+3} ions.

In [1, 5] the values of the nearest neighbour intralayer interaction J_1 and interlayer interaction J_2 have been estimated to be $J_1/k = +3, +7, +6$ K and $J_2/k = -0.8, -0.2,$

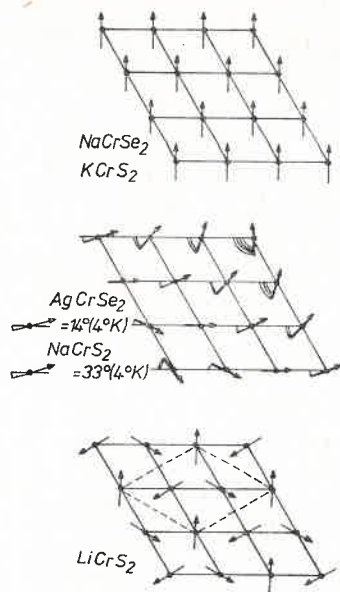


Fig. 2. Basal planes of the magnetic structures of NaCrSe_2 and KCrS_2 (upper figure), AgCrSe_2 and NaCrS_2 (middle figure), LiCrS_2 (lower figure)

-1 K for NaCrS_2 , NaCrSe_2 and AgCrSe_2 , respectively. From these results it follows that the interactions J_2 are so small that metamagnetic properties can be expected [6].

From a $A\text{CrX}_2$ -type compounds the most investigated one was the NaCrS_2 crystal. The ESR line [7, 8], the absorption spectra [9], the magnetic phase diagram, the magnetic shift of the optical band gap, the sublattice magnetization derived from the parallel susceptibility [11], the NMR [12] and the AFMR [10] measurements were performed on this compound.

The angular and temperature dependences of the peak-to-peak width ΔH indicate evidence of ferromagnetic coupling within the planes in NaCrS_2 [7]. The ESR line is Lorentzian at $\theta = 0.55, 90^\circ$ (where θ is the angle between the field and the \hat{c} axis), which is in good agreement with Richard's and Salamon's theory [13].

In NaCrS_2 [8] below 120 K, the linewidth diverges as $(T - T_N)^{-p}$ with $p_{\parallel} = 0.71 \pm 0.01$ and $p_{\perp} = 0.67 \pm 0.05$ parallel and perpendicular to the \hat{c} axis, respectively. The temperature dependent part of the linewidth $\Delta B - \Delta B_{\infty}$ is also proportional to $(T - T_N)^{-p}$ with an exchange of exponent at $T/T_N \cong 1.7$. The observed lineshifts of the ESR line are caused by dipolar fields arising from the bulk magnetization at temperatures down to at least 50 K and by the short-range order within the 10 to 20 K range [8, 11]. In [8] the value of the g factor at room temperature was determined by subtracting the computed dipolar shifts from the observed line as $g_{\parallel} = 1.983 \pm 0.002$ and $g_{\perp} = 1.988 \pm 0.001$ for 36 GHz and $g_{\parallel} = 1.985 \pm 0.002$ and $g_{\perp} = 1.989 \pm 0.001$ for 9.5 GHz.

The ligand field in the NaCrS_2 crystal shows octahedral symmetry with a small trigonal distortion [9]. In this crystalline environment the degeneracy of the ${}^4F_{3/2}$ state is increased, giving a singlet ground state ${}^4A_{2g}$ that remains unsplit, and two excited levels ${}^4T_{2g}$ and ${}^4T_{1g}$. These last two levels are split into 4E_g and ${}^4A_{2g}$ sublevels,

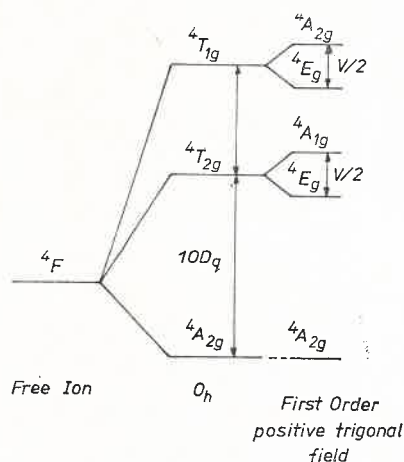


Fig. 3. Energy level diagram for chromium (III) in octahedral and trigonal fields

respectively (Fig. 3). In [9] the first-order trigonal field parameter, the distance between the ${}^4A_{2g}$ and ${}^4T_{2g}$ levels $\Delta = 10Dq$, the Racah parameter B and the nephelauxetic ratio β ($\beta = B/B_0$ where B_0 is the free-ion value of B which for Cr^{+3} ion is 918 cm^{-1}) have been estimated to be: 2500 cm^{-1} , 1400 cm^{-1} , 440 cm^{-1} and 0.480 , respectively. One finds very good agreement of this value of β with $\beta = 0.484$ [14].

The EPR of a Cr^{+3} paramagnetic impurity in NaInS_2 has been also investigated [16, 17]. Resonances were observed for \vec{H} parallel and perpendicular to the \hat{c} axis and between 4.2 and 300 K. The values of the g -factor ($g_{\parallel} \cong g_{\perp}$), the axial parameter $|D|$ were calculated to be: 1.983 ± 0.001 , $0.0362 \pm 0.003 \text{ cm}^{-1}$, respectively. A cation-superhyperfine structure near $g = 2$ was observed for $\vec{H} \perp \hat{c}$ and $\vec{H} \parallel \hat{c}$, and low temperatures. These lines result from the superhyperfine interaction of the unpaired d^3 spins of the transition-metal ion with its six coplanar next-nearest neighbour In^{+3} ions. From the equidistant spacings of the hyperfine lines for $\vec{H} \parallel \hat{c}$ and $\vec{H} \perp \hat{c}$ the interaction constants

have been estimated to be: $A_{\parallel} = 16.6 \pm 0.2$ G, $A_{\perp} = 17.2 \pm 0.2$ G, $\Delta H_{\parallel} = \Delta H_{\perp} = 8$ G. A_{\parallel} and A_{\perp} are not temperature-dependent between 4.2 and 300 K. These data have been analyzed in terms of a three-electron wave function whose components are linear combinations of atomic orbitals of the central Cr^{+3} ion, the six nearest-neighbour sulfur ions, and next-nearest-neighbour coplanar In ions [16]. The g -shift has been discussed, also. It results from two opposing mechanisms: excitation to nonoccupied antibonding orbitals yields negative shifts, and excitation from occupied bonding states to the 4A_2 ground state yields a positive shift. In the case of the $\text{NaInS}_2:\text{Cr}^{+3}$ compound a negative g -shift $\Delta g = -0.013$ was found. This suggests evidence of the first mechanism.

3. Experimental results and discussion

The EPR measurements have been made on the paramagnetic Cr^{+3} ion in NaCrS_2 , NaCrSe_2 , AgCrS_2 , AgCrSe_2 and LiCrS_2 powders with a microwave EPR spectrometer SEX/28 having field modulation at a frequency of 100 kHz. The spectra were recorded in the first derivative absorption line at room temperature and the microwave frequency of 9.4322, 9.4325, 9.4317, 9.435 and 9.4350 GHz, respectively (these values are the averages of the microwave frequency values for a number of measurements performed on each sample in order to test reproducibility of the results). They are very simple since they are composed of one symmetrical line only. Small deviations from the line symmetry are due to the inaccuracy of the spectrometer.

The observed spectra may be described by the spin Hamiltonian:

$$\mathcal{H} = g\beta\vec{H}\vec{S}, \quad (1)$$

where $S = 3/2$ for the Cr^{+3} ion. From the experimental resonance field values the g -factors assigned to the 4A_2 ground state were estimated on the basis of the resonance condition

$$g\beta\vec{H} = h\nu, \quad (2)$$

where β is the Bohr magneton, \vec{H} is the strength of the resonance field, h is Planck's constant and ν is the microwave frequency of the spectrometer. These values are: 1.980, 1.997, 1.968, 1.978 and 1.977 for NaCrS_2 , NaCrSe_2 , AgCrS_2 , AgCrSe_2 and LiCrS_2 , respectively. These values have an inherent experimental error near 15% due to an inaccuracy in the assignment of the line positions. We see that the g -factors are close to the free electron g -value of 2.0023 which suggests the presence of the spin angular momentum of the Cr^{+3} ion effects.

The dipolar interaction effects on the g -shift were calculated with the help of Van Vleck's theory of the line second and fourth moment [18, 19]. The second moment of the EPR line in our case is described by the following equation (for non-identical spins):

$$\langle H^2 \rangle = \frac{4}{15} g^2 \beta^2 S(S+1) \sum_j (1/r_{jk})^6, \quad (3)$$

where $j \neq k$, β is the Bohr magneton, r_{jk} is the distance between spins of the Cr^{+3} and S

or Se ions. In the paramagnetic resonance the six nearest neighbours of the paramagnetic Cr^{+3} ion are responsible for the magnetic absorption and so we take the spin (Cr) \div spin (S or Se) distances only. The exchange interaction does not contribute to the second moment [19]. The second moment of the line $\langle H^2 \rangle$ was calculated from experimental data on the basis of the equation [19]:

$$\langle H^2 \rangle = \frac{B^2}{A} \sum_{j=1}^m \sum_{i=1}^m (H_j - H_0 - B_2)^2 (y'_i - B_1), \quad (4)$$

where A is the area under the curve, B is the spacing of following points on the curve, H_0 is the resonance field, H_j is the field corresponding to the y'_j line-intensity, B_1 and B_2 are corrections to the line position. Equations representing the A , B_1 and B_2 are presented in paper [19]. From the experimental g -values and g -values estimated from equations (3), (4) the g -shifts caused by the dipolar interaction were calculated as: 0.0015, 0.0025, 0.002 for LiCrS_2 , AgCrS_2 and AgCrSe_2 , respectively. The g -shift values for NaCrS_2 and NaCrSe_2 compounds were not calculated since their r_{jk} distances were not known by the author. In [9] the g -shift for the NaCrS_2 crystal has been estimated as 0.002 for g_{\parallel} and 0.001 for g_{\perp} . On this basis the g -shifts for our NaCrS_2 and NaCrSe_2 powders are expected to be of the order of 0.001 \div 0.002. Experimental errors in the calculation of all g -shifts that are due to the spectrometer inaccuracy, the inaccuracy in the assignment of line positions and intensities, are estimated to be near 20%.

In the present paper short range order effects on the EPR line shift were not introduced since they are very small at room temperature and important at low temperatures [20].

Values of the μ_{eff} effective magnetic moment of the A state have been calculated from the experimental g -values to be: $(3.84 \pm 0.003)\mu_B$, $(3.86 \pm 0.003)\mu_B$, $(3.80 \pm 0.004)\mu_B$, $(3.83 \pm 0.004)\mu_B$ and $3.836\mu_B$ for NaCrS_2 , NaCrSe_2 , AgCrS_2 , AgCrSe_2 and LiCrS_2 , respectively. They were compared with the theoretical μ_{eff} -values listed in Table I. The best agreement was found for the LiCrS_2 compound, and small differences between the theoretical and experimental μ_{eff} -values occur for the others. In this case it is imperative to include the exchange coupling and other magneto-optical effects. A small deviation of these μ_{eff} -values from the μ_{eff}^0 pure-spin moment of $3.88\mu_B$ is evidence of a small spin-orbit coupling effect. The shape of the EPR lines for all the compounds was described by the least squares method [21] as nearly Lorentzian. Order of their width at half maximum intensity was estimated as ~ 110 Gs (NaCrS_2), ~ 150 Gs (NaCrSe_2), ~ 440 Gs (AgCrS_2), ~ 415 Gs (AgCrSe_2), ~ 270 Gs (LiCrS_2). This suggests the domination of the exchange interaction of the neighbouring electron spins over the spin-orbit coupling.

Experiments on the ACrX_2 -type monocrystals in a wide temperature range are expected to give more information on the subject (magnetic anisotropy, interesting temperature and position dependence of EPR line, width and position, a possibility of an examination of a dipolar interaction, the bulk magnetization and a short range order effects on the EPR line width, position and shape as function of the temperature and others).

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