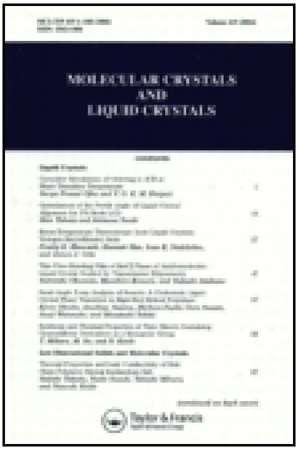

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Electron Spin Resonance In $CuCrS_2$ and $CuCrSe_2$ Single Crystals

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ELECTRON SPIN RESONANCE IN $CuCrS_2$ AND $CuCrSe_2$ SINGLE CRYSTALS

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Abstract Single crystal ESR spectra of $CuCrS_2$ and $CuCrSe_2$ have been measured at both X- and Q-band frequencies. Anisotropic signals from the localised Cr^{3+} d-electrons give zero-field splitting parameters of $0.29cm^{-1}$ and $0.31cm^{-1}$ for the sulphide and selenide respectively, suggesting a possible orbital interaction between the Cr and Cu ions. The dependence of the ESR parameters on temperature shows the effect of magnetic ordering.

$CuCrS_2$ and $CuCrSe_2$ belong to a family of layered chalcogenide compounds of general formula $MCrX_2$, in which M ions are intercalated between sandwich layers of CrX_2. In this family, the magnetic and structural properties of crystals with M = Na, Cu, Ag, Li and X = S, Se have been reported[1,2], the Cu and Ag compounds being isostructural, with Cu(Ag) in slightly distorted tetrahedral sites. All of the compounds known are semiconductors and antiferromagnets with Néel temperatures in the range 19-50K[1-4]. The chromium and intercalate ions have been shown to have nominal oxidation states of +3 and +1 respectively. Electron spin resonance (ESR) measurements have been carried out on the compounds with M = Li, Na and Ag[2,3,5] and all have shown an isotropic signal from the Cr ion (S=3/2) as expected from a ground state of symmetry $^4A_{2g}$ resulting from a trigonally-distorted octahedral crystal field.

In our experiment, ESR measurements were made on single crystals of $CuCrS_2$ and $CuCrSe_2$, using X- and Q-bands at 9.25GHz and 34GHz respectively, and covering the temperature ranges 4-280K and 90-280K respectively. No Cu signal was observed, as expected, but surprisingly the Cr signal in both compounds exhibited a remarkable degree of anisotropy. This anisotropy is illustrated in Figure 1 which shows the experimental variation of resonant field position with orientation for $CuCrSe_2$ at 280K and 9.25GHz. The variation can be used to estimate the zero-field splitting parameter D, which appears in the spin Hamiltonian for the splitting of the Zeeman levels of a spin 3/2 ion in an applied

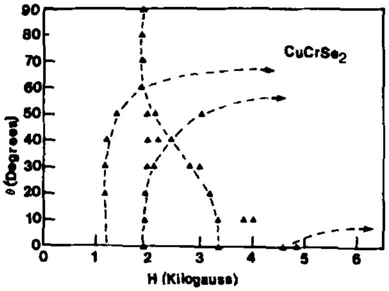


FIGURE 1 Observed variation of X-band resonant field positions with orientation for CuCrSe$_2$ at 280K and 9.25GHz. (θ = 0° corresponds to $B_{/\!/c}$).

field H. In the axially symmetric case the spin Hamiltonian is:

$$\mathcal{H} = \beta\, \underline{H}.\underline{g}.\underline{S} + D(S_z^2 - 1/3\, S(S+1))$$

In this expression, D can be viewed as a measure of the effective distortion of the spin 3/2 site. Weltner[6] and De Biasi et al[7] have computed the variation of the resonant field position with orientation for the allowed ($\Delta m_s = \pm 1$) transitions of an S = 3/2 ion ($g_{/\!/} = g_{\perp} = g_e$, ν = 9.3GHz) over a range of D-values (see Figure 2). Comparison of these values with our X-band data at 280K gives the following estimates:

CuCrS$_2$; D = 0.29cm^{-1}. CuCrSe$_2$; D = 0.31cm^{-1}.

(The assumption $g_{/\!/} = g_{\perp} = g_e$ has been made since for Cr^{3+} ions

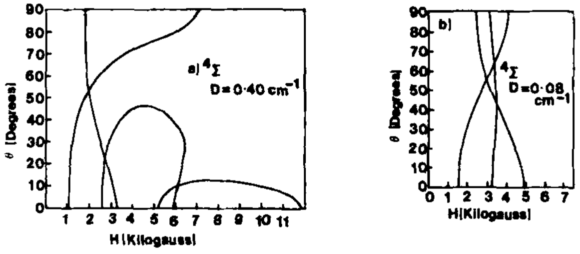


FIGURE 2 Computed variation of allowed ($\Delta m_s = \pm 1$) transitions with orientation for an axially symmetric S=3/2 molecule with a) D = 0.40cm^{-1} and b) D = 0.08cm^{-1}. (After Reference 7).

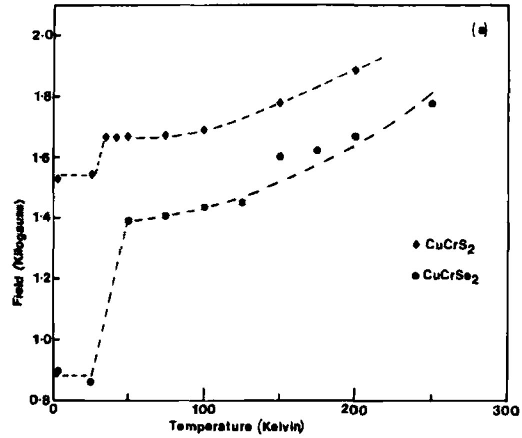
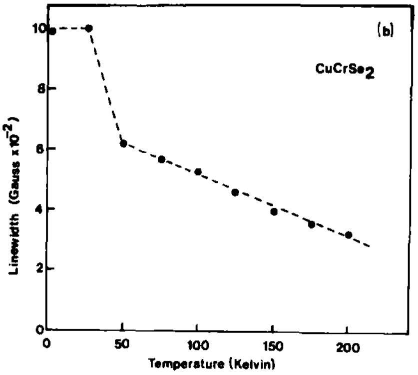


FIGURE 3 a) The variation of resonant field position with temperature for the $\pm\frac{1}{2}$ transition of CuCrS$_2$ and CuCrSe$_2$ ($B_{\perp c}$).



b) The variation of ESR linewidth with temperature for the $\pm\frac{1}{2}$ transition of CuCrSe$_2$ ($B_{\perp c}$).

$g_{/\!/} \simeq g_{\perp} \simeq 1.98$ is usually found[5,8]). The Q-band ESR spectra were consistent with these values of D. The splitting appears to be unique to the Cu members of this family of compounds and suggests that there is an interaction between the Cr and Cu d-orbitals leading to a perturbation of the Cr^{3+} ground state. A situation not unlike this is found in the structurally related spinels, CuCr$_2$S$_4$ and CuCr$_2$Se$_4$, where covalent mixing of the anion p-orbitals and the 3d-orbitals of Cr and Cu, as well as delocalisation of the Cu 3d-orbitals are postulated[9,10].

We have also measured the temperature variation of the ESR line position and width. For both CuCrS$_2$ and CuCrSe$_2$ the resonance moves to lower field and the linewidth increases as the temperature is lowered (see Figure 3). The change in line position arises from both the dipolar field due to bulk magnetisation and the effect of short-range order as the Néel temperature is approached. The increase in linewidth ΔB has been treated thoeretically for a two-dimensional structure and can be described by the relation:

$$\Delta B \propto (T - T_N)^{-p}$$

where theory predicts a value of $p = 0.75$[2]. Our data give a value of 0.4 ($T>T_N$, $B_{\perp c}$) compared to 0.67 which was found for $NaCrS_2$[2]; discrepancies in the exponent have been attributed to different broadening mechanisms. A sharp change in the line position and width marks the transition to a magnetically ordered state confirming Néel temperatures of 39K[1] and 30K[4] for the sulphide and selenide respectively. Below the Néel temperature both the linewidth and the resonant field position remained approximately constant in both compounds.

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