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The Magnetic Structure of $KCrS_2$

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The crystal structure of $KCrS_2$ has been confirmed. Although $KCrS_2$ has been described in the literature as strongly ferromagnetic the magnetic structure consists of ferromagnetic sheets which are antiferromagnetically coupled. The paramagnetic Curie temperature is +112 K, indicating that the ferromagnetic interaction in the sheets is the dominant one.

Introduction

The crystal structure and magnetic properties of $KCrS_2$ have been reported by Rüdorff and Stegemann (*1*). Its space group is $R\bar{3}m(D_{3d}^5)$. Sulfur atoms form a cubic close packing, both the chromium and potassium atoms are located in alternating layers in octahedral holes. The atomic positions, referred to hexagonal axes are:

3 Cr in 3(*a*): 0, 0, 0;

3 K in 3(*b*): $0, 0, \frac{1}{2}$;

6 S in 6(*c*): $\pm(0, 0, z)$ with $z \approx \frac{1}{4}$.

Though $KCrS_2$ is isostructural to $NaCrS_2$, there is a remarkable difference in their magnetic properties as reported in the literature. Rüdorff and Stegemann describe $KCrS_2$ as strongly ferromagnetic with an asymptotic Curie temperature of +116 K. Bongers et al. (*2*) show that $NaCrS_2$, despite its positive θ (+30 K), becomes antiferromagnetic at low temperature, a result which has been confirmed by means of neutron diffraction (*3*).

The present communication reports a new measurement of the magnetic susceptibility of $KCrS_2$ down to 4.2 K and a determination of its magnetic spin arrangement.

Experimental

The powder sample of $KCrS_2$ has been prepared by passing a mixture of H_2S and H_2 over $K_2Cr_2O_7$ at a temperature of about 600°C for several hours (*4*). The resulting product was homogenized and treated again with the H_2S/H_2 mixture at the same temperature. Since $KCrS_2$ is very hygroscopic, all handling must be performed in a dry box.

A chemical analysis of the sample gave the following results:

Cr: 33.53 wt% (theoretical: 33.52 wt%);
S: 39.74 wt% (theoretical: 41.31 wt%);
O: 1.96 wt%.

An X-ray Guinier photograph showed some extra lines which are probably due to $\beta - K_2CrO_4$ and KCr_3O_8.

Neutron diffraction data have been collected at 300 K and 4.2 K on the powder diffractometer at the H.F.R. at Petten. Further experimental details are given elsewhere (*5*). The neutron wavelength was 2.587 Å.

Magnetic susceptibility measurements were carried out at the University of Groningen with a Faraday system constructed by van Bruggen (*6, 7*) and with a vibrating sample magnetometer (Princeton Applied Research), based on the magnetometer described by Foner (*8*).

Susceptibility

The inverse susceptibility of $KCrS_2$ shows a deviation from the Curie–Weiss law at temperatures below ~220 K. Above this temperature the χ^{-1} vs T curve fits a straight line with an asymptotic Curie temperature $\theta = +112$ K and a Curie constant $C_M = 1.96$, roughly corresponding with the expected value $C_M = 1.875$ for three unpaired electrons.

Below $T_N = 38 \pm 1$ K $KCrS_2$ becomes antiferromagnetic as is indicated by the minimum in the χ^{-1} vs T curve (Fig. 1).

From the fact that the above-mentioned deviation from the Curie–Weiss law exists in the temperature region below 5 T_N it can be concluded that up to this temperature a considerable amount of short-range order is present.

Crystallographic and Magnetic Structures

From the neutron diagram at 300 K it was evident that the crystallographic structure as given by Rüdorff and Stegemann (*1*) is correct. The result was not seriously impaired by the fact that also in the neutron diagram the impurities mentioned above were visible.

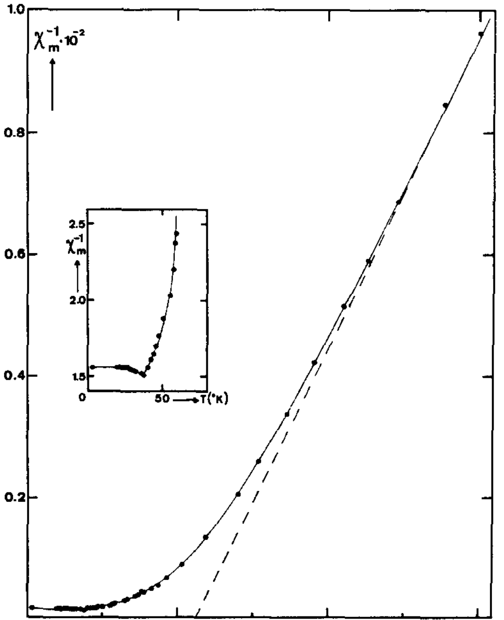

FIG. 1. Temperature dependence of the inverse susceptibility of $KCrS_2$ at a field of 9 kG.

TABLE I

MAGNETIC AND STRUCTURAL PARAMETERS IN $KCrS_2$[a]

Temperature	300 K	4.2 K
a (Å)	3.602(6)	3.601(6)
c (Å)	21.15(5)	21.01(5)
c/a	5.872(2)	5.834(2)
z (S)	0.2741(3)	0.2751(4)
μ_{Cr} (μ_B)	—	3.04(5)

[a] Standard deviations, based on statistics only, are given in parentheses.

The final parameters from a profile refinement (*9*) are given in Table I. The coherent scattering lengths used in the refinement are: $b_K = +0.37 \times 10^{-12}$ cm, $b_{Cr} = +0.3532 \times 10^{-12}$ cm, and $b_S = +0.2847 \times 10^{-12}$ cm.

In the neutron diagram at 4.2 K several extra peaks of magnetic origin became visible which could be indexed by doubling the chemical cell in the c direction. No magnetic contribution to the

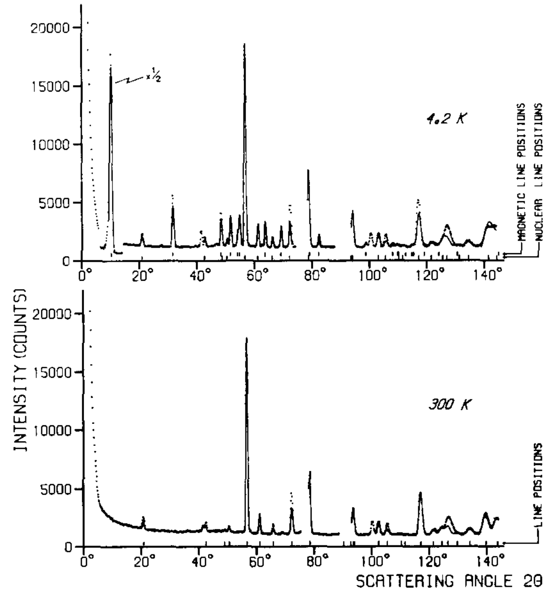

FIG. 2. Observed and calculated neutron diffraction profiles of $KCrS_2$. The dots represent the observed profile, the full line the calculated profile. The angular regions where copper lines of cryostat and sample holder occur (at 76 and 91° 2θ) have been omitted. The peaks at 41.4, 100.3, and 126.8° 2θ are due to impurities.

nuclear peaks was visible. Thus the periodicity of the magnetic lattice is given by a propagation vector in reciprocal space $k = 0,0,\frac{1}{2}$ based on the hexagonal description of the unit cell. From a closer inspection of the diagram it became clear that the magnetic structure consists of ferromagnetic layers perpendicular to the *c* axis which are antiferromagnetically coupled to adjacent layers. As the direction of the moments is also perpendicular to the *c* axis, the orientation of the spins in the layers cannot be determined from powder data.

In Table I the final parameters at 4.2 K based on line profile refinement are given. In the refinement the spherical form factor for Cr^{3+} of Watson and Freeman (*10*) was used. The observed and calculated profiles are shown in Fig. 2.

Discussion

The crystallographic structure as reported by Rüdorff and Stegemann (*1*) has been confirmed.

$KCrS_2$ orders in the same magnetic ordering scheme as the isostructural compound $NaCrSe_2$ (*11*). The paramagnetic Curie temperature ($\theta \approx 112$ K) is of the same order as that in $NaCrSe_2$ (+108 K) and indicates that the ferromagnetic interaction in the planes is the dominant one. It should be noted that the magnetic structure of $NaCrS_2$ is somewhat more complicated, i.e., a helical structure (*3*).

No indication for the existence of a ferromagnetic component in the magnetic structure of $KCrS_2$ is obtained from our neutron diffraction data. Rüdorff and Stegemann (*1*) measured the susceptibility of $KCrS_2$ in fields of 550, 860, and 1040 G; they mention that the samples become strongly ferromagnetic at 90 K. Our measurements show that even in fields of 9 kG $KCrS_2$ is still paramagnetic at 90 K (Fig. 1), but with a large value of χ. Magnetization versus field curves at 4.2 K indicate that $KCrS_2$ becomes ferromagnetic at about 24 kG.

The observed moment of Cr^{3+} in $KCrS_2$ [$3.04(5)\mu_B$] is in good agreement with the expected value of 3 μ_B and with the value from the susceptibility measurements (3.1 μ_B). This can be interpreted as an indication that in $KCrS_2$ covalency effects are weak. In $LiCrS_2$, $NaCrS_2$, $NaCrSe_2$, and $AgCrSe_2$ (*3*, *5*, *11*) the moments observed by neutron powder diffraction are in general considerably less than the expected values indicating that in these compounds covalency effects are not negligible. It should be realized, however, that one must be very careful in making conclusions in too much detail from powder work.

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