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A NEUTRON DIFFRACTION STUDY OF $CuSeO_4$

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Résumé. — La structure antiferromagnétique du sélénate de cuivre anhydre, $CuSeO_4$, a été déterminée par diffraction de neutrons sur poudre. Dans la maille orthorhombique Pbnm, la structure magnétique est colinéaire, de type A (+——+), les spins étant perpendiculaires à l'axe *c*. Le moment magnétique de Cu^{+2} vaut 0,9 ± 0,1 magnétons de Bohr à 7,2 °K, la température de transition 34 °K. Une transformation de phase polymorphique Pbnm → Cmcm plus dense a été observée à 50 kbars, 500 °C.

Abstract. — The antiferromagnetic structure of anhydrous cupric selenate, $CuSeO_4$, has been determined from neutron diffraction powder data. In the Pbnm orthorhombic cell the magnetic structure is collinear of Type A (+——+), with the spin orientation perpendicular to the *c*-axis. The Cu^{2+} moment was found to be 0.9 ± 0.1 Bohr magnetons at 7.2 °K, the transition temperature is 34 °K. A phase transformation of the Pbnm polymorph into the denser structure of symmetry Cmcm was observed at 50 kbars, 500 °C.

Introduction. — The sulfates and selenates of the 3 d-transition elements have been studied extensively and their spin configurations have been established by neutron diffraction techniques [1, 2, 3, 4]. Nevertheless the exchange mechanism in these orthorhombic compounds is not fully understood, and especially $MnSO_4$ with a complicated cycloidal spiral arrangement [4] is unique in this series. The only member not yet studied is $CuSeO_4$, which poses some problems in its preparation, but also difficulties because of the weak magnetic scattering due to the low magnetic moment of Cu^{2+}.

On the other hand $CuSeO_4$ is of specific interest since it crystallizes in two polymorphic forms, one in space group Pbnm and the other in Cmcm, the latter being a high pressure-high temperature polymorph [5]. The difference between Pbnm and Cmcm is a reduction in volume and a different orientation of the SeO_4-tetrahedra, leading to different exchange properties.

Experimental. — Powder $CuSeO_4$ was prepared by dehydration of $CuSeO_4.2\,H_2O$ in air at 300 °C for several hours. The $CuSeO_4.2\,H_2O$ was prepared from $CuCO_3$ and selenic acid. However, the $CuSeO_4$ could not be prepared free from impurities. They are clearly visible on the X-ray diagram, but could not be identified.

Neutron diffraction diagrams were obtained at 77 °K and 7.2 °K with a wavelength of 1.54 Å from a cylindrical sample of pressed pellets of 14 mm diameter and 20 mm high and the structure of the Pbnm-polymorph was determined.

Magnetic Structure. — Due to the low magnetic scattering power of Cu^{2+} only the (001) reflection at $2\theta = 12.7°$ could be unambigously identified in the diffraction diagram at 7.2 °K as arising from magnetic ordering. The isomorphism of $CuSeO_4$-Pbnm with $CuSO_4$-Pbnm, and the similarity of the diffraction patterns lead us to conclude, that $CuSeO_4$ exhibits the same antiferromagnetic structure as $CuSO_4$, which is collinear of type A with (+ − − +) ordering on the Cu^{2+} sites 0 0 0, 0 0 ½, ½ ½ ½, ½ ½ 0 in the Pbnm orthorhombic unit cell. We thus find ferromagnetic coupling within the **ab**-plane, and antiferromagnetic interactions between Cu^{2+} nearest neighbours along the **c**-axis.

As a further argument we have calculated the magnetic moment per Cu^{2+} ion from the observed (001)-reflection. It follows that the spins are lying in the **ab**-plane perpendicular to the **c**-axis. Evaluation of the measured intensity based on the magnetic Cu^{2+}-form factor of $CuSO_4$ given by Cox [6] yields (0.9 ± 0.1) μ_B per Cu^{2+} at 7.2 °K.

Temperature Dependence. — Figure 1 shows the intensity of the magnetic (001) reflection of $CuSeO_4$-Pbnm as a function of temperature indicating an antiferromagnetic transition at 34 °K. The intensity

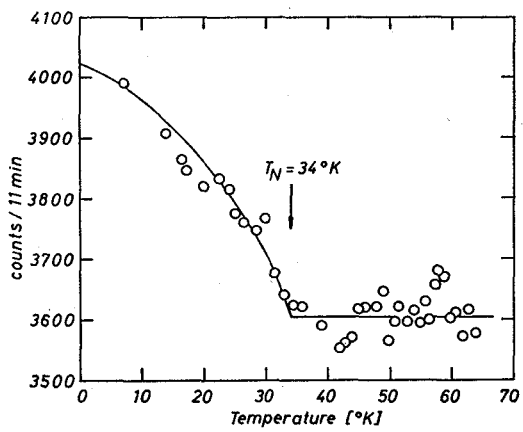

FIG. 1. — Temperature dependence of the intensity of the (001)-magnetic reflection for $CuSeO_4$-Pbnm indicating a Néel point of 34 °K.

variation does not however follow a Brillouin temperature dependence (Fig. 2).

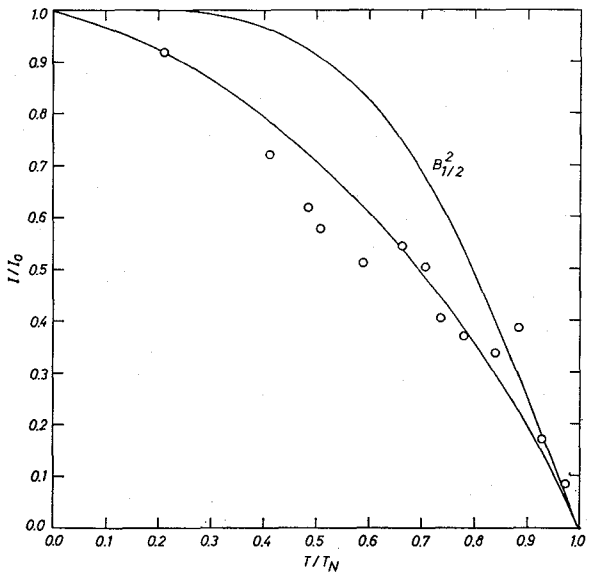

FIG. 2. — Normalized magnetic scattering from (001)-planes of $CuSeO_4$-Pbnm compared with a squared Brillouin dependence for $S = \frac{1}{2}$.

High Pressure. High Temperature Polymorph of $CuSeO_4$. — As reported by Pistorius [5], $CuSeO_4$-Pbnm undergoes a phase transition from Pbnm to Cmcm symmetry at 40 kbars and 400 °C with an especially large volume compression of $\Delta V = 8.7$ %. We expect to get a deeper insight into the exchange mechanism in $CuSeO_4$-$CuSO_4$ by this change in symmetry and super-super-exchange mechanism and we tried therefore to prepare sufficient material for neutron diffraction of the second polymorph. Pressure experiments on a cylindrical sample of 2 mm diameter and 2 mm high at 50 kbars and 500 °C for 1 hour yielded a full transformation of the sample to symmetry Cmcm. Experiments on larger volumes, however, necessary to get the required quantity for neutron diffraction at our research facilities, failed, to give complete transformation of the sample due to the obviously high compressibility of $CuSeO_4$-Pbnm and secondly due to some inevitable pressure gradients in the press. Further experiments are in progress.

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