

³F. A. Jenkins and D. R. Speck, *Phys. Rev.* **100**, 973 (1955).

⁴D. R. Speck, *Phys. Rev.* **101**, 1725 (1956).

⁵Manenkov, Prokhorov, Trapeznikova, and Fock, *Оптика и спектроскопия (Optics and Spectroscopy)* **2**, 470 (1957). (The results pertaining to this reference were reported at the Conference on the Physics of Magnetic Phenomena (Moscow, May 1956) and at the Fifth Conference on Luminescence (Tartu, June 1956)).

⁶B. Bleaney and W. Low, *Proc. Phys. Soc.* **A68**, 55 (1955).

⁷A. A. Manenkov and A. M. Prokhorov, *Dokl. Akad. Nauk SSSR* **107**, 402 (1956); *Soviet Phys. "Doklady"* **1**, 196 (1956).

⁸Manenkov, Prokhorov, Trukhliaev, and Iakovlev, *Dokl. Akad. Nauk SSSR* **112**, 623 (1957); *Soviet Phys. "Doklady"* **2**, 64 (1957).

⁹P. F. A. Klinkenberg, *Revs. Mod. Phys.* **25**, 63 (1952).

¹⁰W. Low, *Phys. Rev.* **103**, 1309 (1956).

¹¹J. S. Van Wieringen, *Physica* **19**, 397 (1953).

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AN ANOMALOUS MAGNETIC TRANSITION IN ANHYDROUS COPPER SULFATE

A. S. BOROVICK-ROMANOV and N. M. KREINES

Institute for Physical Problems, Academy of Sciences, U.S.S.R., and Institute for Technical Physics and Radio Measurements

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We have investigated the magnetic properties of small crystals of anhydrous CuSO_4 from 1.5 to 300°K. Below $T_c = 34.4^\circ\text{K}$ this substance shows antiferromagnetic properties. The transition to the antiferromagnetic state is accompanied by an anomalous, twofold increase of the susceptibility in a temperature interval of about 1.5°.

IN a previous paper¹ we investigated the temperature dependence of the magnetic susceptibility of anhydrous copper sulfate in the temperature range from 14 to 300°K. At $T = 35^\circ\text{K}$ the susceptibility showed a sharp increase, corresponding to a change of 30% over a temperature interval of about 2°K. A further lowering of the temperature was accompanied by a smoother increase of the susceptibility. The specimen of anhydrous copper sulfate we used in that experiment was obtained by heating copper sulfate to 300° C for two hours with constant stirring (see Ref. 2). All operations were performed in a current of dry nitrogen. The specimen was obtained in the form of a light blue, very hygroscopic powder.

Our investigations at helium temperatures have shown that the increase of the susceptibility which is observed below 35°K is apparently caused by the presence of paramagnetic impurities. The most likely impurity to be present can be assumed to be some singly hydrated copper sulfate. An approximate estimate showed that in the specimen used by us there could be found 20% singly hydrated copper sulfate.

The specimens of anhydrous copper sulfate used by us in the present experiment were obtained in two ways. The first specimen was obtained from a solution of copper sulfate in molten ammonium sulfate.³ Above 360°C $(\text{NH}_4)_2\text{SO}_4$ decomposes and anhydrous copper sulfate remains in the form of a precipitation. In this case the specimen was obtained in the form of small transparent crystals of $1 \times 0.2 \times 0.2$ mm,

with a faint blue color. These crystals were far less hygroscopic than the powder used by us in the first experiment.*

In Fig. 1 we have shown the two most successful of the crystals obtained in this way. We hope, after improving our methods slightly, to investigate the anisotropy of magnetic properties with these crystals.

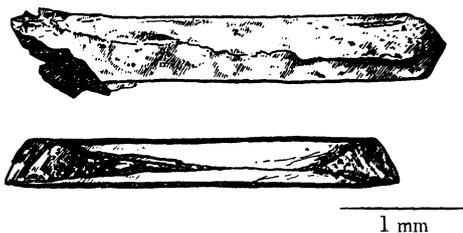


FIG. 1. Crystals of anhydrous CuSO_4 .

The second specimen was obtained by annealing copper sulfate at 270°C until its weight was constant. The vessel with the specimen was evacuated both before and after the heating, since the material lost 5 molecules of water. If we pump continuously during the annealing the specimen decomposes before the complete dehydration has taken place.

We measured the magnetic susceptibility of anhydrous copper sulfate, obtained by the first method, in the range of temperatures between 1.5 and 300°K . The measurements were performed in an apparatus similar to the one described in Ref. 4.

From Fig. 2, which gives the temperature dependence of the reciprocal of the molar susceptibility, we see that in the temperature range from 300 to 120°K a Curie-Weiss law with $\Theta = -77.5^\circ$ and $C = 0.517$ is followed. Below 120°K we observe a deviation from the straight line corresponding to the Curie-Weiss law. In the same

figure we have drawn the results of the measurements by de Haas and Gorter⁵ on anhydrous copper sulfate, which agree reasonably well with ours.

In Fig. 3 we have given the temperature dependence of the molar magnetic susceptibility of CuSO_4 . At about 35°K the susceptibility rises sharply, changing almost by a factor of two in a temperature interval of about 1.5 degrees. At 34.4°K the susceptibility attains a maximum and then falls to a value which is $3/4$ of its maximum value. Starting at about 12°K down to 1.5°K the susceptibility stays constant. In the region where the susceptibility rises steeply it depends on the value of the magnetic field.

One can see in Fig. 4 that an

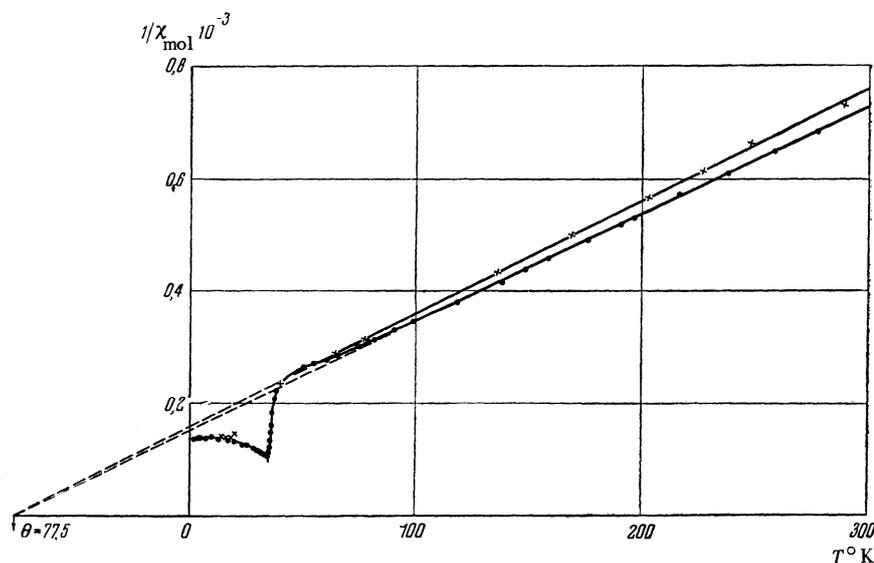


FIG. 2. Temperature dependence of the reciprocal of the molar magnetic susceptibility $1/\chi_{\text{mol}}$ of anhydrous copper sulfate. \times — results from Ref. 5; \bullet — our results.

increase in the magnetic field produces a fall in the susceptibility while its maximum is displaced towards lower temperatures. The maximum change in the susceptibility observed by us was about 10% when the field was changed from 3,400 to 13,000 oersted. The results obtained with the second specimen were similar to the ones just described except in the temperature range from 4 to 1.5°K where the susceptibility slightly increased. Such a behavior of the susceptibility is apparently produced through an insufficient dehydration of the specimen.

The results which we have obtained for the temperature dependence of the magnetic susceptibility of anhydrous copper sulfate show that at 34.4°K this material undergoes a transition below which it apparently becomes antiferromagnetic. The transition itself is unusual and differs from the normal ones by an anomalously steep rise of the susceptibility in the neighborhood of the transition. The question as to the character of the transition remains for the time being an open one.

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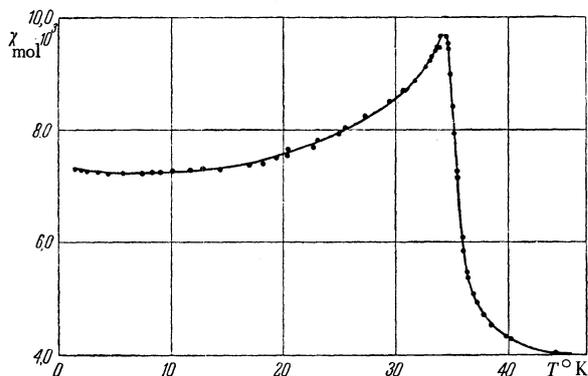


FIG. 3

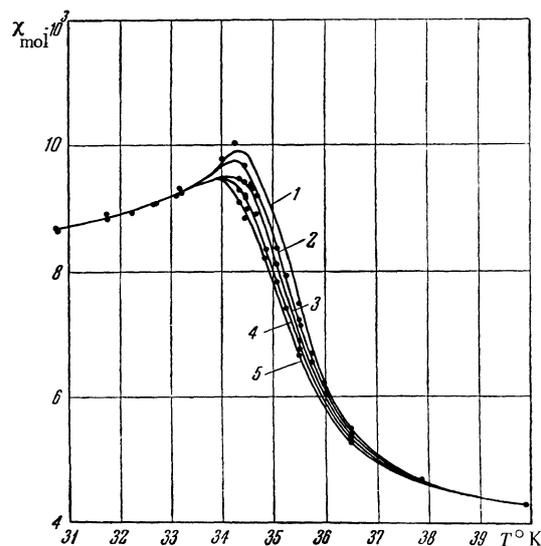


FIG. 4

FIG. 3. Temperature dependence of the molar magnetic susceptibility χ_{mol} of anhydrous copper sulfate.

FIG. 4. Temperature dependence of the molar magnetic susceptibility χ_{mol} of anhydrous copper sulfate in the transition region for different intensities of the magnetic field: 1 — 3,370; 2 — 6,660; 3 — 9,700; 4 — 11,780; 5 — 12,900 oersted.

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¹Borovik-Romanov, Karasik, and Kreines, J. Exptl. Theoret. Phys. (U.S.S.R.) **31**, 18 (1957), Soviet Phys. JETP **4**, 109 (1957).

²Iu. V. Kariakin and I. I. Angelov, Чистые химические реактивы (Pure Chemical Reagents) Goskhimizdat, Moscow, 1955.

³M. P. Klobb, Compt. rend. **114**, 836 (1892).

⁴A. S. Borovik-Romanov and N. M. Kreines, J. Exptl. Theoret. Phys. (U.S.S.R.) **29**, 790 (1955), Soviet Phys. JETP **2**, 657 (1956).

⁵W. J. de Haas and C. J. Gorter, Leiden Commun., 215a, 1931; Proc. Roy. Acad. Sc., Amsterdam **34**, 317 (1931).

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