ANOMALY IN THE MAGNETIC ANISOTROPY OF $K_3Fe(CN)_6$ *SINGLE CRYSTALS AT LOW TEMPERATURES*

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The anomalous behavior in the magnetic anisotropy of $K_3Fe(CN)_6$ single crystals near 126°K, apparently due to the interaction between paramagnetic ions, is described.

THE temperature dependence of the anisotropic magnetic susceptibility of $K_3Fe(CN)_6$ single crystals has been studied experimentally[1-4] and theoretically[5-7] by a number of investigators. The new measurements reported in this paper were motivated by the recently published paper of Stephenson and Morrow[8] in which an anomaly in the specific heat of $K_3Fe(CN)_6$ was reported at 131°K. The authors attribute this anomaly to a magnetic transition of some kind but do not consider the effect in detail.

All the presently available measurements of the magnetic anisotropy in $K_3Fe(CN)_6$ single crystals at low temperatures have been performed over large temperature ranges[1, 2, 4] or have not included the temperature indicated above.[3] In no case has there been a detailed investigation in the temperature region in which the specific-heat anomaly has been observed. Moreover, the experimental results reported by different authors are not consistent. Up to this time no account has been taken of x-ray studies of the structure of $K_3Fe(CN)_6$ carried out by Barkhatov and Zhdanov,[9-11] although these would be useful in interpreting the experimental results. In addition paramagnetic resonance measurements carried out in recent years[12, 13] furnish valuable new data which should be exploited. Inasmuch as potassium ferricyanide serves as a classical example of a so-called covalent complex, it is hoped that the present work will be of value.

EXPERIMENTAL RESULTS

Large $K_3Fe(CN)_6$ single crystals were grown in water solutions; a few especially well-formed crystals were used. The morphology of potassium ferricyanide crystals is described by Groth.[14] The crystal structure has been studied by Barkhatov and Zhdanov.[9-11] The elementary cell contains two parts by weight of $K_3Fe(CN)_6$. The relation between the external crystallographic axes (a, b, c), the molecular axes (α, β, γ) and the molecular magnetic axes (x, y, z) in the ab plane are shown in Fig. 1. These crystallographic data were used in analyzing the magnetic anisotropy.

The measurements of the magnetic anisotropy were carried out by the Krishnan technique, using the system which has been described in detail in reference 15; this system can be used to measure the anisotropies over small temperature ranges (1 to 2 degrees) in the temperature region 90 to 300°K. Thus, it was possible to make a detailed study of the region near 130°K of interest to us. The strength of the uniform magnetic field was measured by a nuclear-resonance method. The torsional constant of the quartz fiber was determined by measuring the torsional period of a suspended body whose moment of inertia was known. The crystals were suspended and measured along all three crystallographic axes; this procedure was necessary since the angle between the crystallographic and magnetic axes in potassium ferricyanide is temperature dependent, especially at low temperatures. The difference between the results of the present measurements and the paramagnetic-resonance measurements[13] and the results obtained by Guha[4] is explained by the fact that this factor was not taken into account.

To compute the magnetic susceptibilities along all three magnetic axes one must know the temperature dependence and the mean value of the susceptibility. These measurements were performed at the same temperatures using the method described by Guha.

The results of measurements of the magnetic susceptibilities χ_1, χ_2, and χ_3 and the mean susceptibility are shown in Fig. 2. Although the measurements were performed at every 2 or 3 degrees, for clarity the points in the figure are

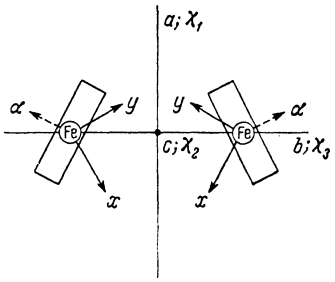

FIG. 1

given at every 10 degrees, except for the points of interest in the neighborhood of the transition. As is apparent from the figure, χ_1 and χ_3 are essentially the same at the higher temperatures. This result indicates that the tetragonal crystallographic field predominates in potassium ferricyanide. Frequently, there is a rotational effect when the crystals are suspended by the c axis since it is difficult to determine the position of this axis accurately from the external shape of the crystal. As we have already indicated, the crystals must be measured in all directions; that is to say, we must have more measured quantities than there are unknowns in the computation formulas. It is necessary to eliminate the uncertainty in the determination of the crystallographic axes. The positions of the magnetic axes with respect to the external axes of the crystal (a, b, c), the molecular axes in the elementary cell (α, β, γ) and the molecular magnetic axes (x, y, z) in the ab plane are shown in Fig. 1. The magnetic axes of the crystal coincide with the crystallographic axes. The molecular magnetic axes x and y form angles of 30 and 60 degrees with the magnetic axis χ_1 in the ab plane. The molecular magnetic z axis is perpendicular to the χ_1 and χ_3 axes and is parallel to the χ_2 axis; thus, this axis is perpendicular to the plane of the figure.

The most interesting results of these measurements are those for the temperature dependence of the magnetic anisotropy near 126°K. As is apparent from Fig. 2, at this temperature χ_1 increases considerably, χ_2 decreases, and χ_3 remains unchanged. Measurements by the Guha method in polycrystalline samples, show a discontinuity at this same temperature in the slope of the susceptibility-vs.-temperature curve. The existence of this anomaly in the magnetic anisotropy was verified many times in several crystals. The measurements in the transition region are not as accurate as those at the other points because there was a temperature variation during the measurement. This variation was a result of the large angle of rotation of the quartz fiber. It is difficult to determine the location of the peak. However, the effect is so large that there can be no doubt as to its existence. The absolute accuracy in the temperature measurements is ± 2°; the relative accuracy for the series of measurements is ±0.5°. The error in the measurements is due chiefly to the fact that the temperature is not measured in the crystal itself, but rather in the vicinity of the crystal.

It is interesting to note that after the anisotropy transition the magnetic axis χ_3, which is along the crystallographic axis, is characterized by a higher magnetic susceptibility than the χ_1 axis. A change in the direction of the axis of highest magnetization has been also observed by Bleaney and O'Brien[7] in paramagnetic-resonance measurements.

DISCUSSION OF THE RESULTS

The anomaly in the magnetic anisotropy in the present work is observed at approximately the same point as the anomaly in the specific heat which has been observed by Stephenson and Morrow in polycrystalline potassium ferricyanide. The present measurements verify the assumption made by these authors that the anomaly is due to a magnetic transition. Furthermore, we have shown that the transition is anisotropic. Since it is almost entirely compensated along the χ_1 and χ_2 axes the effect on the mean magnetic susceptibility and specific heat is very small.

It is difficult to interpret this anomaly on the basis of the experimental and theoretical data available at this time. Bleaney and O'Brien have observed in paramagnetic-resonance measurements that the highest susceptibility is along the a axis at 90°K and along the b axis at 20°K.

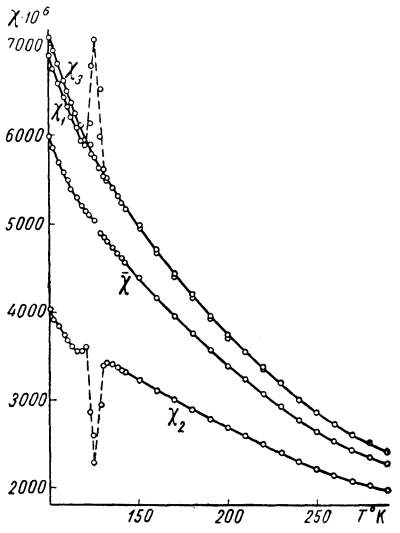

FIG. 2

The effect observed by these authors is not characteristic of diamagnetic dilution; hence, it is reasonable to assume that the effect is due to exchange interactions between neighboring paramagnetic ions. Apparently the anomaly reported here is of the same nature. It would seem that the interaction between magnetic ions in the present case is highly anisotropic and is related to the change in direction of the magnetic axes of the individual molecules. This is to be associated with a change in the direction of the axes of the crystal as a whole. A theoretical analysis indicates that in $K_3Fe(CN)_6$ a small change in the crystalline field must lead to a marked change in the anisotropy.[7] The exchange forces between neighboring paramagnetic ions are found in ions with five or more d-electrons.

The problems considered here have been studied recently in many experimental and theoretical papers concerned with problems in antiferromagnetism.[16] The relation between the effects reported here and this work will be examined in subsequent papers.

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