number for the ions Ti I to Ni VII. Separations for the ^5F level obtained from the alternative classification seem to fit this $(\Delta\nu)^{\frac{1}{2}}$ graph better than do those obtained from Bowen's classification, which are indicated by crosses. Final substantiation will have to await the identification of further combinations or intercombinations with the ^5F terms.

In conclusion, the authors wish to express their appreciation to Mr. C. E. McClellan for his assistance in making the wave-length measurement.

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The Magnetic Anisotropy of Copper Sulphate Pentahydrate, $CuSO_4\cdot 5H_2O$, in Relation to its Crystal Structure. Part III.

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Measurements have been made of the magnetic anisotropy of $CuSO_4\cdot 5H_2O$ at different temperatures from 26°C to −190°C. The crystal is nearly uniaxial magnetically, and its two principal susceptibilities conform roughly to the Curie law, with different Curie constants. The observed anisotropy of the crystal may be attributed to the anisotropy induced in the Cu^{++} ion under the influence of the asymmetric electric field of the neighboring negatively charged atoms. From the known positions of these atoms the field should be expected to have tetragonal symmetry. The two principal susceptibilities of the Cu^{++} ion, along the tetragonal axis of the field, and perpendicular to the axis, respectively, are calculated. The corresponding effective magneton numbers are calculated therefrom, and it is found (1) that these magneton numbers vary little with temperature, and (2) that the magneton numbers corresponding to the two principal susceptibilities of the ion are widely different.

1. Introduction

In Parts I and II[1] of this paper we gave an account of some magnetic studies on $CuSO_4\cdot 5H_2O$ at room temperature, and a discussion of the results in relation to the structure of the crystal. The results verify in a striking manner the views advanced by Van Vleck,[2] and Penney and Schlapp[3] regarding the origin of magnetic anisotropy in a paramagnetic crystal, namely that it is due to the asymmetry of the internal electric fields acting on the paramagnetic ions in the crystal. The crystal of $CuSO_4\cdot 5H_2O$ is triclinic and its unit cell contains two Cu^{++} ions. Each of these ions is in the center of an octahedron formed by six negatively charged oxygen atoms.[4] The octahedron is not regular, but may be regarded as derived from a regular one by drawing out symmetrically one of its diagonals. This diagonal will thus be an axis of tetragonal symmetry for the octahedron, and therefore also for the electric field acting on the Cu^{++} ion located at the center of the octahedron. Now the tetragonal axes of the two octahedra in the unit cell make with each other an angle of 82°. We should therefore expect the internal and the external bisectors of this angle, and the normal to the two bisectors, to be the three principal magnetic axes of the crystal. The susceptibility along the first direction should be the maximum for the crystal, and that along the third the minimum; and further, since the angle between the two tetragonal axes is nearly a right angle, the intermediate susceptibility should be nearly the same as that along the first direction, i.e., should be close to the maximum. All these results deduced from the structure of the crystal are verified experimentally.

Denoting the susceptibility of the Cu^{++} ion along the tetragonal axis of the field acting on it by $K_{\parallel}$, and that perpendicular to the tetragonal axis by $K_{\perp}$, we find that at 26°C, $K_{\parallel}-K_{\perp}=550\times 10^{-6}$ per gram ion, and that the mean susceptibility $K=(K_{\parallel}+2K_{\perp})/3$ at this temper-

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[1] Krishnan and Mookherji, Phys. Rev. **50**, 860 (1936) and **54**, 533 (1938).

[2] Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford, 1932).

[3] Penney and Schlapp, Phys. Rev. **41**, 194 (1932).

[4] Beevers and Lipson, Proc. Roy. Soc. **A146**, 570 (1934).

ature is about 1520×10^{-6} (equal to the mean susceptibility of the crystal, corrected for its diamagnetism). The anisotropy of the Cu^{++} ion in the crystal is thus about 36 percent of its mean susceptibility, and it points to a strong asymmetry in the crystalline field acting on Cu^{++}.

The present paper deals with the temperature variation of the anisotropy and the principal susceptibilities of the crystal, and of the principal susceptibilities, $K_{\parallel}$ and $K_{\perp}$ of the Cu^{++} ion in it, from the temperature of the room to that of liquid air. The earlier theories are shown to be inadequate to explain the temperature variation of the anisotropy, and the results are considered on the basis of Van Vleck's theory.

2. The Curie-Weiss Law

The magnetic behavior of paramagnetic ions in crystals naturally differs from that of the free ions. The most striking departures are the magnetic anisotropy exhibited by the crystal, and the deviations of the temperature variations of the principal susceptibilities from the Curie law.[5] These were explained on the older theories as arising from certain internal magnetic fields, which were presumed to be of the same nature as the inner fields in ferromagnetics, and were taken to be proportional to the intensity of magnetization. On this basis the temperature variations of the three principal susceptibilities are given by the simple formulae

$$\chi_i = C/(T-\Theta_i)\,; \qquad i=1,\,2,\,3\,; \tag{1}$$

the Curie constant C, which is determined by the magnetic moment of the paramagnetic ion, which is assumed to be capable of turning around freely in the crystal, will naturally be the same for all the three directions, while the Θ's which are determined by the internal magnetic fields developed in the presence of the applied field, may depend on the direction of the latter in the crystal. When the Θ's are small, the mean susceptibility of the crystal, i.e., the powder susceptibility, will also conform to a formula of the same type,

$$\chi = (\chi_1+\chi_2+\chi_3)/3 = C/(T-\Theta), \tag{2}$$

where

$$\Theta = (\Theta_1+\Theta_2+\Theta_3)/3. \tag{3}$$

Coming back to the crystal of $CuSO_4\cdot5H_2O$, its susceptibility in the powder state has been measured by de Haas and Gorter[6] over a wide range of temperatures, from 14° to 290°K, and it conforms closely to the formula

$$\chi = 0.456_9/(T+0.70), \tag{4}$$

where χ refers to one gram ion.

The temperature variation thus approximates practically to the Curie law, and the value of 0.456_9 for the Curie constant gives for the magnetic moment of Cu^{++} 1.92 Bohr magnetons, as compared with the theoretical value of 1.73 for the single spin moment. These results would suggest, on the basis of these older theories, (1) that the inner magnetic fields are very feeble; and (2) that as in many other salts of the iron group, the contribution from the orbital angular momentum of the paramagnetic ion to the observed magnetic moment is small. We should then expect the anisotropy of the crystal to be small, and the temperature variations of the three principal susceptibilities to conform to formula (1), in which the Θ's should be small, and the Curie constant C should have the same value, namely about 0.457, for all the three principal directions.

We have already seen that the anisotropy of the crystal is by no means small. We shall show presently that the principal susceptibilities also do not conform to Eq. (1).

3. Experimental

The general method adopted in the present measurements is the same as that described by us and Mr. Bose in a recent paper.[7] The main part of the apparatus is the cryostat for maintaining the temperature of the crystal constant at any desired value. The crystal is suspended freely inside a thin-walled copper tube, closed at the bottom, and immersed deeply in a liquid

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[5] If the higher multiplet levels of the paramagnetic ion, being low, are also occupied, and the magnetic moments corresponding to these levels differ from that of the ground state, e.g. Eu^{+++}, Sm^{+++}, the temperature variation of the susceptibilities of even the free ions may deviate from the Curie law, but in a manner that may be readily predicted.

[6] de Haas and Gorter, Leiden Comm. 210 d (1930).

[7] In course of publication in Phil. Trans. Roy. Soc. London.

bath of petroleum ether of boiling point 30°–50°C. The temperature of the bath was controlled automatically by a constant volume air-thermometer, of thin-walled copper, immersed in the bath. When the temperature of the bath rises above the desired value, the air in the thermometer expands and closes the electric circuit of an air-pump which slowly sucks liquid air into a small copper vessel immersed in the bath and thus cools it. When the temperature of the bath falls below the desired value, the air in the thermometer contracts, the electric current through the air-pump circuit is cut off automatically, and that through a small heating coil, also immersed in the cryostatic bath, is made, and the temperature of the bath rises. In practice the two circuits, through the air-pump and the heating coil respectively, alternate in quick succession, and the temperature remains steady to within 0.1°C.

Below about −140°C the petroleum ether becomes very viscous, and temperatures lower than this cannot be maintained with the above arrangement. The only temperatures lower than this at which measurements are made are those of liquid oxygen or air, used as bath liquid instead of the petroleum ether, and allowed to evaporate at atmospheric pressure. The electrical connections for temperature control are cut off in this arrangement.

All the temperature measurements are made with a calibrated copper-constantan thermocouple.

The magnetic measurements are made in the same manner as in Part II. The suspension for the crystal, however, now consists of two parts. The upper part is a calibrated quartz fiber, which remains at room temperature always, and its torsional constant is therefore independent of the temperature of the cryostat; and the lower part is a much stouter fiber which may be regarded as practically rigid.

4. Results

Measurements of magnetic anisotropy are made for five different suspensions of the crystal, which are numbered in the same manner as in Parts I and II; suspensions (2), (7) and (8) which correspond to low anisotropies, are omitted in the present measurements. The results are given in Tables I to V.

Suppose the torsion-head has been adjusted such that the torsion on the quartz fiber may be zero when the crystal has taken up its natural orientation in the magnetic field, namely with the direction of the maximum susceptibility for the crystal in the horizontal plane along the field. Let us call this position of the torsion-head its zero-position. Let α_0 be the angle through which the torsion-head has to be rotated from the above zero position so as to bring the crystal just to its unstable orientation in the field. Let us denote by λ the quantity $\Delta\chi \cdot mH^2/(2Mc)$, where m is the mass of the crystal, M is its molecular weight, H is the magnetic field, c is the constant of torsion of the suspension fiber, and $\Delta\chi$ is the difference between the maximum

TABLE I. *Suspension (1): 'c' axis vertical.* $(\bar{1}00)$ *sets at* $27°+\epsilon$, *and* $(\bar{1}\bar{1}0)$ *at* $53°+\epsilon$, *to the field;* ϵ *increases from 0 at room temperature to 1.5° at 82°K.* $\Delta\chi=183\times10^{-6}$ *at 299°K.*

Temp. °K	304.9	270.8	251.8	231.5	210.7	194.5	170.2	148.2	137.8	90.1	81.5
ρ	0.98	1.10	1.16	1.26	1.38	1.51	1.68	1.95	2.02	3.01	3.26

TABLE II. *Suspension (3):* $(\bar{1}00)$ *and* $(\bar{1}11)$ *vertical.* $(\bar{1}00)$ *sets at* $45\frac{1}{2}°$, *and* $(\bar{1}11)$ *at 14°, to the field; except at the two lowest temperatures, where the setting angle differs from the above by about 1°.* $\Delta\chi=263\times10^{-6}$ *at 299°K.*

Temp. °K	295.8	270.6	248.7	231.0	211.6	194.5	189.4	174.3	148.1	90.1	82.0
ρ	1.01	1.08	1.14	1.22	1.33	1.46	1.48	1.59	1.86	2.87	3.00

TABLE III. *Suspension (4):* $(\bar{1}\bar{1}0)$ *and* $(\bar{1}11)$ *vertical.* $(\bar{1}\bar{1}0)$ *sets at* $62\frac{1}{2}°$, *and* $(\bar{1}11)$ *at* $9\frac{1}{2}°$, *to the field, at all the temperatures.* $\Delta\chi=264\times10^{-6}$ *at 299°K.*

Temp. °K	271.1	251.9	231.8	211.0	194.5	171.1	143.1	90.1	83.0
ρ	1.08	1.14	1.23	1.33	1.45	1.63	1.95	2.90	3.08

TABLE IV. *Suspension (5): (100) horizontal: 'c' axis sets at* $59°+\epsilon$, *and the intersection of* $(\bar{1}00)$ *and* $(\bar{1}11)$ *at* $8°-\epsilon$, *to the field;* ϵ *increases from 0 at room temperature to* $\frac{1}{2}°$ *at 90°.* $\Delta\chi=146\times10^{-6}$ *at 299°K.*

Temp. °K	304.9	271.4	251.0	230.2	210.1	194.5	176.0	158.9	148.4	90.1
ρ	0.99	1.08	1.13	1.23	1.33	1.42	1.52	1.67	1.77	2.70

TABLE V. *Suspension (6): (110) horizontal. 'c' axis sets at* $44°+\epsilon$, *and the intersection of* $(\bar{1}\bar{1}0)$ *and* $(\bar{1}11)$ *at* $12\frac{1}{2}°-\epsilon$, *to the field;* ϵ *increases from 0 at room temperature to 2° at 90°K.* $\Delta\chi=213\times10^{-6}$ *at 299°K.*

Temp. °K	271.4	250.2	231.1	211.0	194.5	190.5	170.1	149.8	90.1
ρ	1.09	1.14	1.21	1.33	1.41	1.44	1.60	1.77	2.71

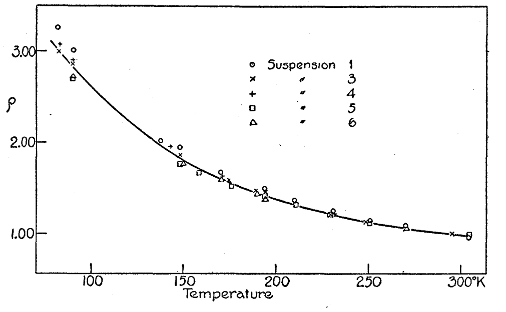

FIG. 1.

and the minimum susceptibilities of the crystal in the horizontal plane, per gram molecule. The quantity λ is connected with the observed critical angle α_0 by the relation (see Part II)

$$\lambda=(\alpha_0-\pi/4-\sigma)/\cos 2\sigma \tag{5}$$

where

$$\sin 2\sigma=1/(2\lambda). \tag{6}$$

From observations on α_0 at different temperatures with the suspension and the field the same, we can calculate with the help of relations (5) and (6) the corresponding values of λ.

The quantity ρ in the tables denotes the ratio of the value of λ at any given temperature to that at 26°C. Obviously, this will also be the ratio of the anisotropies $\Delta\chi$ at the two temperatures.

The values of ρ for the different suspensions are plotted against temperature in Fig. 1.

5. SOME GENERAL FEATURES OF THE TEMPERATURE VARIATION OF THE ANISOTROPY OF THE CRYSTAL

An examination of the data entered in the above tables, shows firstly that the setting directions are practically independent of temperature; the largest variation as we pass from room temperature to that of liquid air is only 2°; and secondly that the value of ρ at any given temperature is more or less the same for all the five suspensions. This is exhibited clearly in Fig. 1, where the experimental points for all the suspensions are seen to lie close to the mean curve; the values for suspension (1) lie slightly above the curve, and those for the suspensions (5) and (6) slightly below it.

We may conclude from these results that the principal magnetic axes of the crystal are practically the same at all the temperatures. We have seen that at room temperature the crystal is nearly uniaxial magnetically, and the axis makes with the *a*, *b* and *c* axes of the crystal angles of 154°, 64° and 51°, respectively. Denoting the susceptibilities along the axis and perpendicular to it by $\chi_{\parallel}$ and $\chi_{\perp}$, respectively, we found in Part II that at room temperature, namely 299°K, $\chi_{\perp}-\chi_{\parallel}=275\times10^{-6}$. The present measurements show that at the other temperatures also, the crystal will remain approximately uniaxial, and the direction of the axis will remain the same; and the anisotropy $\chi_{\perp}-\chi_{\parallel}$ may be taken to be roughly equal to $\rho\times275\times10^{-6}$, where ρ is the value obtained from the mean curve plotted in Fig. 1. The values of $\chi_{\perp}-\chi_{\parallel}$ given in Table VI were obtained in this manner.

Combining these data with the values for the mean susceptibility, $\chi=(\chi_{\parallel}+2\chi_{\perp})/3$, obtained by de Haas and Gorter, we can calculate the principal susceptibilities of the crystal, $\chi_{\parallel}$ and $\chi_{\perp}$, separately, at different temperatures. These

TABLE VI. *Principal susceptibilities of copper sulphate pentahydrate crystal.*

Temp. °K	ρ	$(\chi_{\perp}-\chi_{\parallel})\times10^6=275\rho$	$\chi=(\chi_{\parallel}+2\chi_{\perp})/3\times10^6$	$\chi_{\parallel}\times10^6$	$\chi_{\perp}\times10^6$	$\chi_{\parallel}(T-2.0)$	$\chi_{\perp}(T+1.8)$
299	(1.00)	275	1525	1342	1617	0.399	0.486
280	1.06	291	1628	1434	1725	0.399	0.486
260	1.12	308	1753	1548	1856	0.399	0.486
240	1.19	327	1899	1681	2008	0.400	0.485
220	1.28	352	2070	1835	2187	0.400	0.485
200	1.40	385	2277	2020	2405	0.400	0.485
180	1.54	424	2529	2246	2670	0.400	0.485
160	1.72	473	2844	2529	3002	0.400	0.486
140	1.95	536	3248	2891	3427	0.399	0.486
90.1	2.84	781	5032	4511	5292	0.398	0.486
						mean = 0.399	0.486

calculated values are also entered in Table VI. All the χ's have been corrected for the diamagnetism of the crystal. The anisotropy of the diamagnetism of the crystal, as judged from the observed anisotropy of diamagnetic sulphates,[8] should be negligible.

As will be seen from the figures given in the last two columns of the table, the two principal susceptibilities of the crystal conform closely to the formulae

$$\chi_{\parallel}=0.399/(T-2.0) \tag{7}$$

and

$$\chi_{\perp}=0.486/(T+1.8). \tag{8}$$

Though both of them are of the Weiss type, the Curie constants for the two directions are widely different, a result which, as we mentioned before, is not expected on the Weiss theory.

Since the Θ's are small, the mean susceptibility also naturally obeys a formula of the same type. It is easily verified that Eqs. (7) and (8) lead to expression (4) for the mean susceptibility, as they should.

6. THE PRINCIPAL SUSCEPTIBILITIES OF THE CUPRIC ION IN THE CRYSTAL

Viewing these results on the basis of Van Vleck's theory, we can calculate the anisotropy, $K_{\parallel}-K_{\perp}$, of the Cu^{++} ion in the crystal, due to the asymmetry of the crystalline electric field acting on it. Since the field has tetragonal symmetry, and the tetragonal axes of the fields acting on the two Cu^{++} ions in the unit cell are nearly perpendicular to each other, we have the simple relation (see Part II)

$$K_{\parallel}-K_{\perp}=2(\chi_{\perp}-\chi_{\parallel}), \tag{9}$$

from which $K_{\parallel}-K_{\perp}$ is known at different temperatures. Since further $K_{\parallel}+2K_{\perp}=\chi_{\parallel}+2\chi_{\perp}$ (the χ's, as we mentioned before, denote the principal susceptibilities of the crystal, which have been corrected for its diamagnetism), we can calculate from the data given in Table VI, the values of $K_{\parallel}$ and $K_{\perp}$ separately, at different temperatures. The results are given in Table VII.

TABLE VII. *The effective Bohr magneton values of the magnetic moment of the* Cu^{++} *ion in the copper sulphate pentahydrate crystal.*

Temp. °K	$K_{\parallel}\times10^6$	$K_{\parallel}(T+4\cdot5)$	$n_{\parallel}$	$n_{\perp}$
299	1892	0.574	2.13	1.80
280	2016	0.574	2.13	1.80
260	2164	0.572	2.13	1.80
240	2335	0.571	2.12	1.80
220	2539	0.570	2.12	1.80
200	2790	0.571	2.12	1.80
180	3094	0.571	2.12	1.81
160	3475	0.572	2.12	1.81
140	3963	0.573	2.11	1.81
90.1	6073	0.574	2.10	1.81
		mean = 0.572		

Since evidently $K_{\perp}=\chi_{\parallel}$, and the values for $\chi_{\parallel}$ have already been given, the values for $K_{\perp}$ have not been entered in the table.

Let us denote the effective Bohr magneton values of the magnetic moment of the Cu^{++} ion when the applied magnetic field is along the tetragonal axis of its crystalline field, and when it is perpendicular to it, by $n_{\parallel}$ and $n_{\perp}$, respectively;

$$n_{\parallel}^2/K_{\parallel}=n_{\perp}^2/K_{\perp}=3kT/(N\beta^2), \tag{10}$$

where $\beta=eh/4\pi mc$ is the Bohr magneton, N is the Avogadro number and k is the Boltzmann constant. The values of $n_{\parallel}$ and $n_{\perp}$, calculated from $K_{\parallel}$ and $K_{\perp}$ in relation (10), are also given in Table VII.

The most striking feature of the anisotropy of the Cu^{++} ion under the crystal fields is that whereas the effective magneton numbers for both the principal directions of the field vary little with temperature, showing that both the principal susceptibilities of the Cu^{++} ion obey practically the Curie law of inverse dependence on T, the magneton numbers for the two principal directions are widely different. To be more precise, the two principal susceptibilities of the ion conform to the formulae

$$K_{\parallel}=0.572/(T+4.5) \tag{11}$$

and

$$K_{\perp}=0.399/(T-2.0), \tag{12}$$

with small Curie temperatures, and widely different Curie constants.

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[8] Krishnan and Banerjee, Phil. Trans. Roy. Soc. **A235**, 343 (1936).