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Variation of the Principal Magnetic Susceptibilities of Certain Paramagnetic Crystals with Temperature

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Curie and Weiss Constants for the Principal Susceptibilities of Certain Crystals. The Curie and Weiss constants, respectively C_m and Δ of the equation $x_m = C_m/(T+\Delta)$, over the temperature range 60° to -45°C have been determined for 5 crystals of the isomorphic monoclinic double sulphate series $[\mathrm{M\ R_2(SO_4)_2\ 6H_2O}]$ containing cobalt, nickel, or copper, and for cobalt sulphate heptahydrate. The measurements were made by Rabi's method of determining the principal magnetic susceptibilities of crystals, which was found applicable over this temperature range. The use of ethyl alcohol as a solvent for the auxiliary paramagnetic salt permitted the extension of the method to temperatures below the freezing point of water solutions, such as those used by Rabi, for crystals of volume susceptibilities less than 35×10^{-6}. The lower limit of the applicability of the method depends only on the availability of low freezing point solutions of sufficient susceptibility. In general the Curie constants for the principal susceptibilities of any given crystal were very nearly the same. The Weiss constant showed considerable variation, both between the different principal magnetic axes of the same crystal, and from one crystal to another. Both the Curie and Weiss constants decreased progressively as the metal ion was changed from cobalt to nickel to copper. The effect of change in the alkali ion from NH_4 to potassium was less pronounced, although there was a slight tendency for the Curie constant to increase and for the Weiss constant to become more positive. The accuracy claimed for the measurements is 1 percent. In general there was a small continuous change in the orientation of the principal magnetic axes in the plane of symmetry of the crystal with respect to the crystallographic axes as the temperature was varied.

INTRODUCTION

A NUMBER of investigators have made measurements by various methods of the principal magnetic susceptibilities of crystals. An interesting set of crystals is the isomorphic monoclinic double sulphate hexahydrate series, upon which very complete crystallographic and optical data have been obtained by Tutton.[1] The principal susceptibilities of several members of this series have been measured by Fincke[2] and by Jackson.[3] There is considerable disagreement between the results of these two investigators for the same members of the series. Using a quite different method, Rabi[4] has determined the principal susceptibilities of a large number of crystals of this series. His method has two intrinsic advantages over those of the other investigators;

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[1] A. E. H. Tutton, Proc. Roy. Soc. London **A88,** 361 (1913); Phil. Trans. Roy. Soc. **A216,** 1 (1916).

[2] W. Fincke, Ann. d. Physik [4] **31,** 149 (1910).

[3] L. C. Jackson and H. Kamerhigh Onnes, Phil. Trans. Roy. Soc. **A224,** 1 (1923); Proc. Roy. Soc. **A104,** 671 (1923); L. C. Jackson, Phil. Trans. Roy. Soc. **A226,** 107 (1927).

[4] I. I. Rabi, Phys. Rev. [2] **29,** 174 (1927).

it requires no accurate knowledge of the fields and field gradients involved, and it permits a direct measurement of the orientation of the principal axes of susceptibility with respect to the crystallographic axes.

The present paper is concerned primarily with the effects of temperature upon the principal susceptibilities. It also serves, however, as a further check on the values already obtained at room temperatures. A comparison of existing results with those obtained during this research will be given later.

Jackson[3] has made measurements on two crystals of the double sulphate series over a considerable range of temperatures. Due to the disagreement between his values and those of Fincke and Rabi at room temperatures it was considered desirable to repeat these measurements over as wide a range as possible by Rabi's method, in addition to measurements on members of this series not previously investigated over a range of temperatures. The need for accurate data of this kind has been enhanced by recent advances in the quantum theory of susceptibilities.[5,6]

Method

In Rabi's method[4] of measuring the principal susceptibilities of crystals the crystal is suspended from a torsion head by a glass fibre so as to lie in the inhomogeneous part of the field of a Weiss magnet, in the position shown in Fig. 1. In this position it rests in a solution, the susceptibility of which may be varied at will by the addition of a strongly paramagnetic salt. In general the direction of the field and that of the resulting intensity of magnetization in the crystal will not coincide. In this case displacement of the crystal will result, no matter what the susceptibility of the solution, when the field is applied. If, however, the crystal is so oriented that either its axis of maximum or minimum susceptibility in the XY plane is parallel to the field, the directions of field and resulting intensity in the plane coincide. In this case if the susceptibility of the solution is the same as that of the crystal in the direction of the field, the resultant force on the crystal is zero and it suffers no displacement. For mathematical demonstration of this statement and those which follow the reader is referred to Rabi's paper. It should be noted that the foregoing statement applies to the axes of maximum and minimum susceptibility in the XY plane, these being 90° apart.

In the special case where the direction of one of the principal axes of susceptibility is known, the crystal may be suspended parallel to this direction, and then the other two principal axes will automatically lie in the XY plane. This is the case with monoclinic crystals, in which one principal axis coincides with the symmetry axis of the crystal. In this case the three principal susceptibilities and the orientation of the axes may be determined very simply and directly. The crystal is suspended parallel to its symmetry axis, the torsion head turned and the susceptibility of the solution varied until no displacement of the crystal occurs when the field is applied. The value of one of the

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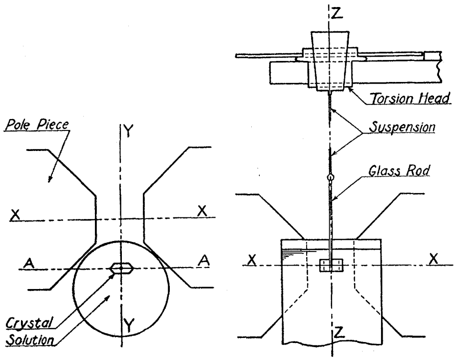
[5] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, New York, 1932.

[6] O. M. Jordahl, W. G. Penney, and R. Schlapp, Phys. Rev. [2] **40**, 637 (1932).

principal susceptibilities in the plane of symmetry is then directly equal to that of the solution, which may be measured very simply by the well-known Gouy method.[7] The crystal is then rotated through 90° and the susceptibility of the solution again varied until no displacement takes place, determining the other principal susceptibility in the symmetry plane. The crystal is next suspended perpendicular to the symmetry axis, rotated until this axis is parallel to the field, and the susceptibility of the solution is then varied as before until there is no displacement. The susceptibility of the solution is then equal to that of the third principal axis. In practise, displacement of the crystal along the X and Y axes of the magnet (Fig. 1) is observed independently. Motion along the Y axis is governed by the susceptibility of the solution, and along the X axis largely by the angular orientation of the crystal about the axis of suspension. The procedure is therefore simply to turn the crystal until there is no motion along the X axis when the field is applied, and then to vary the susceptibility of the solution until displacement in the Y direction is eliminated.



PLAN

ELEVATION - SECTION AA

Fig. 1. Method of suspension of crystal.

The angle which the maximum axis of principal susceptibility in the plane of symmetry of the crystal makes with one of the crystallographic axes, say the c axis, may be obtained directly as follows. The orientation of the c axis of the crystal is first determined with respect to the X axis of the magnet by reflecting a beam of light back on itself from a known face of the crystal along the Y axis of the magnet. The angle through which the crystal must be turned to obtain a balance with the solution with either its maximum or minimum principal axis parallel to X is then read from the torsion head. Since the angle which the c axis makes with X is determined from this reading and its previous orientation, the angle between the c axis and the principal axis is also given. It is assumed throughout that the glass fibre is stiff enough not to allow the crystal to twist with respect to the torsion head.

The sensitivity of the measurement of the orientation of the principal axes is high. Displacement of the crystal in the X direction for any given field

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[7] E. C. Stoner, *Stoner, Magnetism and Atomic Structure,* E. P. Dutton, New York, p. 40 (1916).

strength is a function of the difference between maximum and minimum susceptibility in the XY plane. It is greater when the axis of minimum principal susceptibility is being balanced, and in the case of crystals for which the difference in principal susceptibilities is 10 percent or more it is considerable even if the crystal is away from balance by only one degree. Observation is simplified by the fact that the displacement along the X axis changes direction as the crystal is rotated from one side of the equilibrium position to the other.

This method of determining principal susceptibilities is independent of the shape of the crystal, provided it is not too large. It does not, therefore, require the grinding of crystal sections of definite shape and orientation with respect to the crystallographic axes. This discussion has been limited to the application of the method to monoclinic crystals. It is, however, perfectly general, although in the most general case a greater number of observations and somewhat more complicated calculations are required.

Experimental Procedure

The experimental procedure followed in this research was essentially the same as that described in Rabi's paper. Certain minor modifications were made necessary to permit measurements to be made satisfactorily over the temperature range. Two magnets were used, one for the comparison of the crystals with the solution, and one for the determination of the susceptibilities of the solutions by the Gouy method. While this arrangement facilitates the measurements under any conditions, it is essential with hot and cold solutions that the two measurements be made as nearly simultaneously as possible to prevent change in the solution, either by evaporation, condensation, or precipitation.

The crystals were suspended from a torsion head graduated in degrees by glass suspensions about 30 cm long and 5 mils in diameter. It was found that Rabi's method of attaching the crystals to the suspension with molten shellac was impracticable at the higher temperatures, as the shellac softened and the crystals dropped off. The same thing occurred at all temperatures when alcohol was used as a solvent, as might be expected. After considerable experimentation with other adhesives, it was finally found necessary to drill a properly oriented hole through each crystal, and suspend it upon a slightly tapered glass rod inserted through the hole and attached in turn to the suspension. The diameter of the hole thus drilled was in general less than 10 mils and the rods used had a maximum diameter of about this value. The holes were drilled by hand with a jeweler's drill, and after a little practise it was found easily possible to orient them within one or two degrees of the desired direction.

Motion of the crystals was observed by means of two microscopes focussed on the rods just as they came out of the solution. Both microscopes had scales in their eyepieces, and in particular that used for observing motion in the Y direction had sufficient magnification to detect displacement of 0.002 cm, which was less than the random motion of the crystals due to convection currents in the solution. The solution was contained in a Dewar flask inserted in the angle of the pole pieces so as to permit the crystal to be suspended in a reasonably strong gradient. Temperatures were measured to half a degree by means of a standard thermometer graduated in tenths. This was sufficiently accurate for the balance of crystal and solution, the critical temperature measurement being that made when the solution was being measured by the Gouy method.

To ensure constancy of temperature during the measurement of the susceptibility of the solution the magnet used for this purpose had a jacketed brass tube inserted between its pole pieces. The jacket was connected to a coil run through a three gallon bath, and constant temperature was maintained by pumping water or alcohol through the system. For temperatures above the room the bath was water heated by an immersion heater, and for low temperatures it was alcohol or alcohol and water cooled with solid carbon dioxide. Fig. 2 shows diagrammatically the arrangement of the jacket. The whole investigation was carried on in a double walled constant temperature room to ensure constancy of temperature of the magnet throughout.

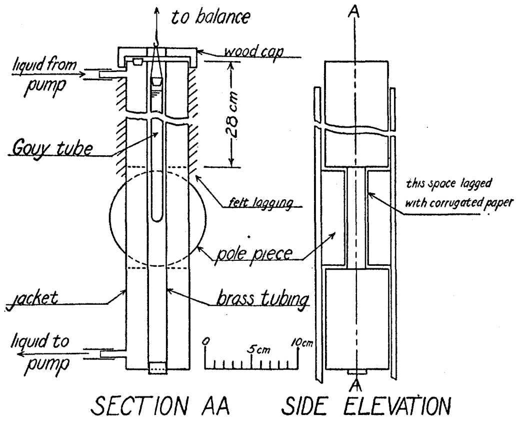

Fig. 2. Diagram of temperature control jacket.

The Gouy tubes used were of Pyrex glass, approximately 30 cm long and 1 cm in diameter. They were suspended from a chainomatic balance, sensitivity 0.05 mg, located well out of the field, which had no detectable influence upon the balance or suspension. The Gouy tubes were calibrated with distilled water, -0.720×10^{-6} being taken as standard for the susceptibility of water.[8]

Temperatures of the solutions were measured by the insertion of a thermocouple into the tube containing the solution at the time of measurement. Constancy of temperature during the measurement was checked by means of another couple inserted through the walls of the jacket into the inside of the brass tube in which the Gouy tube was suspended. As there was a slight

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[8] Int. Crit. Tables, Vol. **VI**, p. 356.

gradient in the Gouy tube, care was taken to measure the temperature at the point where the field gradient was a maximum.

For measurements at room temperatures and above water solutions were used, saturated with respect to the material of the crystal. Susceptibilities were varied by the use of manganous chloride, the amount of this salt in the solution being varied as necessary to balance the crystal. The maximum temperatures at which measurements could be made by this method were limited in general by the disturbance of the solution due to convection currents, although in the case of cobalt sulphate heptahydrate change in the chemical state set the limit. Obviously the lower limit to the method is the freezing point of the solution. In general with water solutions freezing started, or at least the solution became too thick for precise observations, in the neighborhood of $-25°C$. Accordingly search was made for satisfactory solvents of lower freezing point. Experimentation with alcohols, acetone, and other organic liquids of low freezing point resulted in the choice of ethyl alcohol as solvent and anhydrous manganous chloride as solute. This combination gave the largest volume susceptibility of those tried, about 35×10^{-6}, a value sufficiently high for all the crystals except those containing cobalt. For the latter the lower limit was therefore the freezing point of the water solutions. The use of the alcohol solution extended the range to $-45°C$ for the copper and nickel crystals. Below $-50°C$ the alcohol solutions became so viscous as to prevent further measurements.[9]

CRYSTALS

The crystals measured were $Co\ (NH_4)_2(SO_4)_26H_2O$, $Co\ K_2(SO_4)_26H_2O$, $Co\ SO_4\ 7H_2O$, $Ni\ (NH_4)_2(SO_4)_26H_2O$, $Cu\ (NH_4)_2(SO_4)_26H_2O$, $Cu\ K_2(SO_4)_2\ 6H_2O$. Of these the hexahydrates are of the isomorphous monoclinic series so thoroughly investigated crystallographically by Tutton.[1] The two containing cobalt have been investigated magnetically by Jackson[3] over a considerable range of temperatures. Cobalt sulphate heptahydrate is also monoclinic, and has been investigated crystallographically by Marignac,[10] and magnetically by Fincke[2] at room temperatures. The mean susceptibilities of all these salts, in powdered form, except those containing copper have been measured over a wide range of temperatures by Jackson.[3]

Some of the crystals were grown by slow cooling and some by evaporation. Only materials of tested purity were used, and all the crystals selected for measurement had been recrystallized at least twice for further purification. Further check on the purity of the specimens was provided by using at least 6 different crystals for each set of measurements and rejecting any which varied by more than two percent from the mean value. It was found that

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[9] Work is in progress at Columbia University on the susceptibilities of these and other crystals at liquid air temperatures. Paramagnetic and diamagnetic liquids offer no difficulties at these temperatures, since liquid oxygen is paramagnetic and liquid nitrogen is diamagnetic, and they are miscible in all proportions. For measurements at intermediate temperatures special liquids would have to be found.

[10] C. de Marignac, Mem. Soc. Phys. Genève **14**, 245 (1858); C. F. Rammelsberg, Hdb. d. Kr-Phys. Chem. **1**, 419 (1881).

great care was required in selecting crystals without flaws or cloudiness if consistent results were to be obtained. In this connection it is suggested that some of the disagreement in published results may have come from the use of imperfect crystals. The writer found that some crystals which were perfect in outward appearance gave out small amounts of saturated liquid when pierced by the drill, indicating imperfect crystallization within the core of the crystal. In general the crystals used were about 0.5 cm on an edge.

It was found necessary to wash the crystals very carefully after each measurement to prevent any manganous chloride drying out of the solution onto the crystal. If this was not done errors of five percent or more were introduced into the results. As a check on the care with which this was done each set of crystals was measured again at room temperature at the completion of the temperature run.

In addition to the measurements on the individual crystals a check on the general consistency of the results was obtained by making a run on powdered crystals by the Gouy method. The accuracy of such measurements was limited by the uniformity with which the powders could be packed into the tube. Also the measurement of temperature was not so accurate as with the solutions, as the temperature of the powder could not be read directly, but had to be determined from dummy tubes held at the same jacket temperatures for the same lengths of time. These measurements however serve as a check against any gross errors in the individual measurements.

ACCURACY

The absolute accuracy of the method of the present investigation is definitely limited by the accuracy of the standard value for the susceptibility of water, which is probably about 0.5 percent. In the present work the sensitivity of the null balance of crystal against solution was of the order of 0.1 percent except in the case of the crystals containing copper, for which it was about $\frac{1}{4}$ percent. The sensitivity of the gravitational balance was 0.1 percent or better. The measurement of temperature had a precision of 0.2°, and allowing for temperature gradient in the tube was probably accurate to better than 0.5°. The couples used were calibrated against standard thermometers and against the freezing point of mercury. The field of the Gouy method magnet was checked for constancy by a meter with a precision of 0.1 percent. The magnet itself was in a constant temperature room, and its temperature did not vary by more than one or two degrees throughout the investigation. Heating of the magnet by the current used was highly improbable, as the currents were well below the capacity of the magnet, and were on only for comparatively short time intervals. Further check on this fact is afforded by the fact that the currents were remarkably constant, indicating no heating of the coils.

The insertion of the glass rod through the crystal introduces a systematic error approximately equal to the ratio of the volume of the rod in the solution to the volume of the crystal. From the geometrical dimensions involved this error was in all cases well under 0.5 percent.

Probably the most serious source of error, aside from impurities and irregularities in the crystals themselves, was that which might arise from change in the solution between the balancing of the crystal and the measurement of the susceptibility of the solution. To get the solution from the Dewar flask into the Gouy tube in general required from one to two minutes. To prevent precipitation from the solution the temperature of the bath and the solution had to be very closely the same. By working rapidly results could be checked to about $\frac{1}{4}$ percent at any temperature, although the precision of the check was better the closer the temperature of the solution was to that of the room. While in the Gouy tube the solutions were enclosed with a stopper to prevent evaporation or condensation. In calibrating the Gouy tubes correction for the susceptibility of air was necessary. From the foregoing, the

TABLE I. *Principal susceptibilities.* Axes 1 and 2 refer respectively to the maximum and minimum principal susceptibilities in the plane of symmetry of the crystal, axis 3 to the principal susceptibility perpendicular to this plane. Temperatures are given in degrees centigrade. K is the volume susceptibility, x the mass susceptibility, and x_m' the molecular susceptibility corrected for diamagnetism.

Crystal	T	$K\times10^6$			$x\times10^6$			$x_m'\times10^6$		
		1	2	3	1	2	3	1	2	3
$Co(NH_4)_2(SO_4)_2$-$6H_2O$	55.0	50.4	38.1	44.8	26.5	20.0	23.6	10660	8080	9500
	20.0	58.3	41.5	50.5	30.7	21.8	26.6	12300	8790	10690
	3.0			53.5			28.2			11320
	−3.5	64.1	44.4		33.7	23.4		13480	9430	
	−11.0			56.4			29.7			11900
	−20.0	69.3	46.8	58.9	36.4	24.6	31.0	14570	9900	12440
$CoK_2(SO_4)_26H_2O$	55.0	52.2	41.1	44.0	23.5	18.6	19.8	10460	8330	8840
	20.0	58.6	44.9	48.6	26.4	20.2	21.9	11720	9010	9750
	0.0	63.5	47.7		28.6	21.5		12690	9580	
	−5.0			51.7			23.3			10360
	−20.0	67.8	50.2	54.6	30.5	22.6	24.6	13500	10060	10930
$CoSO_47H_2O$	45.0			59.5			30.5			8700
	40.0	67.3	55.9		34.5	28.6		9830	8170	
	21.0	71.8	59.4	63.9	36.8	30.4	32.8	10470	8680	9350
	0.0	76.4	63.0	67.9	39.2	32.3	34.8	11150	9210	9910
	−15.0			71.6			36.7			10440
	−20.0	81.7	67.2		41.9	34.5		11920	9830	
$Ni(NH_4)_2(SO_4)_2$-$6H_2O$	51.0	18.75	18.23	18.47	9.74	9.47	9.59	4030	3920	3970
	21.0	20.62	20.12	20.02	10.72	10.48	10.40	4420	4320	4290
	−15.0	23.11	22.57	22.46	12.03	11.75	11.66	4930	4820	4790
	−42.0	25.65	25.20	25.28	13.37	13.10	13.15	5460	5350	5370
$Cu(NH_4)_2(SO_4)_2$-$6H_2O$	53.0	6.35	5.17	6.13	3.30	2.69	3.18	1500	1257	1452
	19.0	7.27	5.81	7.02	3.78	3.02	3.65	1692	1388	1640
	−5.0	7.97		7.65	4.14		3.97	1837		1768
	−9.0		6.49			3.37			1528	
	−45.0	9.55	7.53	9.26	4.96	3.91	4.81	2163	1743	2103
$CuK_2(SO_4)_26H_2O$	55.0	6.62	5.24	6.26	2.96	2.34	2.80	1490	1215	1420
	22.0	7.47	5.90	7.10	3.34	2.64	3.18	1658	1349	1587
	−15.0	8.51	6.78		3.81	3.04		1865	1523	
	−45.0	9.71	7.72	9.16	4.35	3.46	4.10	2105	1710	1998

Note: It may be wise to emphasize here that the actual experimental results obtained by the method of this paper are the volume susceptibilities.

agreement of the writer with the results of Rabi, and the general consistency of the results, it appears reasonable that the values of susceptibility given in this paper are accurate to 1 percent, and that their relative accuracy is somewhat greater, probably of the order of 0.5 percent.

The measurements of the angle between the maximum axis of principal susceptibility and the crystallographic c axis are probably accurate to 1°[4] and consistent to $\frac{1}{2}$°, except in the case of the nickel crystal, for which the sensitivity of angle measurement was very low with the fields available, about 2°.

RESULTS

Table I gives the results of the measurements of the principal susceptibilities of the various crystals, including volume susceptibilities, mass susceptibilities, and molecular susceptibilities corrected for diamagnetism. Each value is the average of several individual crystals, in most cases six. The average deviation in no case exceeded 1 percent, and in all except a very few cases was less than $\frac{1}{2}$ percent. Table II gives the angle, θ, which the maximum axis of principal susceptibility in the symmetry plane makes with the c crystallographic axis. Fig. 3 shows the symmetry plane of the double sulphates, and Fig. 4 that of cobalt sulphate heptahydrate. Table III gives the Curie and Weiss constants for the crystals. Figs. 5, 6, and 7 show curves of the reciprocal of the molecular susceptibilities corrected for diamagnetism plotted against absolute temperature.

TABLE II. *Orientation of principal susceptibilities.* The numbers in this table are the values in degrees of the angle, θ, which the maximum axis of principal susceptibility in the plane of symmetry makes with the c crystallographic axis. θ is measured positive in the direction of the acute angle between the c and a crystallographic axes.

Crystal	Temperature in degrees centigrade									
	55	50	45	40	30	20	0	−10	−20	−45
$Co(NH_4)_2(SO_4)_26H_2O$	−43½					−43½			−43½	
$CoK_2(SO_4)_26H_2O$	−14					−13	−12½		−11½	
$CoSO_47H_2O$			*−56½			−55½	−54½		−53½	
$Ni(NH_4)_2(SO_4)_26H_2O$		−13				−17			−21	−23
$Cu(NH_4)_2(SO_4)_26H_2O$		−87	−84	−83	−81	−79		−76		−72½
$CuK_2(SO_4)_26H_2O$	−101¾					−102½			−104	−105

* Above this point a large and variable change in angle indicated a change in the state of the crystal. This change was accompanied by a corresponding change in susceptibilities, and a distinct change in the appearance of the crystal, probably due to dehydration.

TABLE III. *Curie and Weiss constants.* In the following table the Δ's and the C_m's are those of the Weiss formula $x_m' = C_m/(T+\Delta)$, in which x_m' is the molecular susceptibility corrected for diamagnetism and T is the temperature in degrees Kelvin.

Crystal	Δ_1	Δ_2	Δ_3	C_{m1}	C_{m2}	C_{m3}
$Co(NH_4)_2(SO_4)_26H_2O$	−50	81	−10	2.9	3.3	3.0
$CoK_2(SO_4)_26H_2O$	5	88	67	3.5	3.5	3.4
$CoSO_47H_2O$	23	44	45	3.3	2.9	3.2
$Ni(NH_4)_2(SO_4)_26H_2O$	30	25	25	1.42	1.36	1.36
$Cu(NH_4)_2(SO_4)_26H_2O$	−9	24	−2	0.475	0.44	0.47
$CuK_2(SO_4)_26H_2O$	14	20	18	0.51	0.425	0.49

Correction for diamagnetism included that for water of crystallization, the alkali molecule, and the sulphate ion of the metal molecule, and totalled 180×10^{-6} for the double sulphates and 100×10^{-6} for cobalt sulphate heptahydrate. The values used were those given in the International Critical Tables, vol. IV, page 365. In the case of crystals containing cobalt and nickel the diamagnetic correction is small compared with the total susceptibilities. In the case of the copper crystals, however, it becomes considerable, 15 percent in the extreme. This undoubtedly introduces some uncertainty into the values of the Curie and Weiss constants for these crystals, as the accuracy of the diamagnetic correction may be held in question. There is no certainty

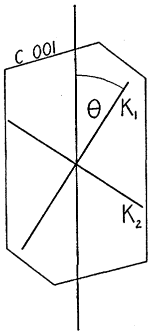

Fig. 3. Plane of symmetry of double sulphate crystals.

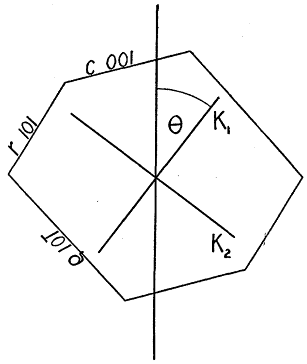

Fig. 4. Plane of symmetry of cobalt sulphate heptahydrate.

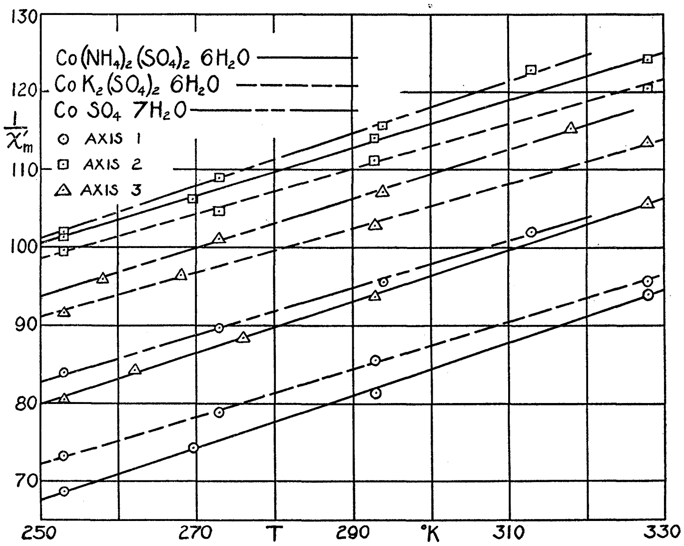

Fig. 5. Curves of $1/\chi_m'$ against temperature for crystals containing cobalt.

that the linking of the components in the complex molecule does not alter the commonly accepted values of the ionic susceptibilities, and there is further no inherent reason that the diamagnetic correction is the same along

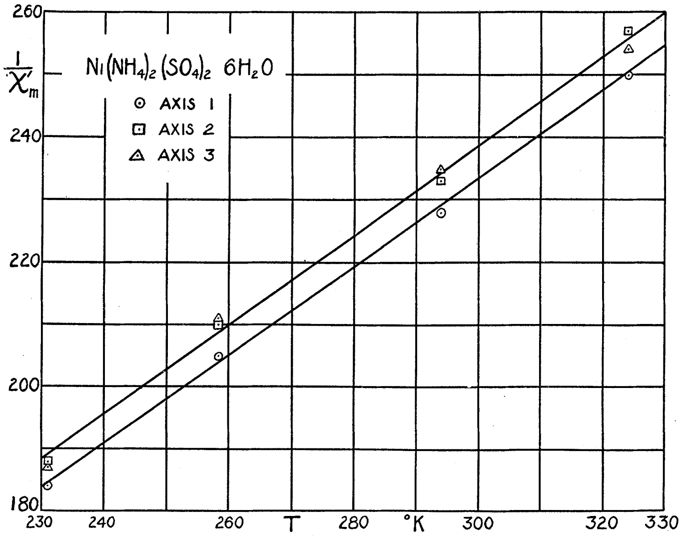

Fig. 6. Curves of $1/x_m'$ against temperature for nickel ammonium sulphate.

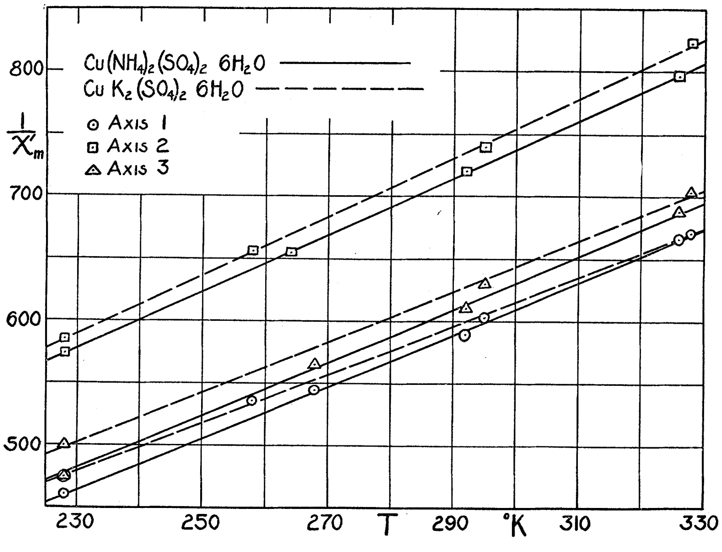

Fig. 7. Curves of $1/x_m'$ against temperature for crystals containing copper.

each axis, as has been assumed in making the correction for want of data on the subject.

The results of Table I have not been corrected for the volume expansion of the crystals with temperature. This will introduce some error into the mass and molecular susceptibilities given in the table. Values for the coefficient of volume expansion of these crystals are not available, at least to the knowledge of the writer. Coefficients of volume expansion for crystals such as $MgSO_47H_2O$ and $CuSO_45H_2O$ as given in the International Critical Tables, vol. III, page 44, are, however, all less than 10^{-4} per °C. In the extreme case this would entail a correction of about 1 percent in the mass susceptibilities. The effect of this correction would be to increase the Curie constants slightly, and to make the Weiss constants all slightly more positive. Table IIIA gives values of these constants corrected for an assumed coefficient of volume expansion of 10^{-4} per °C. Additional evidence that this correction is small is furnished by the measurements on the powdered crystals. In this case mass susceptibilities are measured directly, so that if the effect is appreciable it should show up when the mass susceptibilities of the powders are compared

TABLE IIIA. *Curie and Weiss constants corrected for volume expansion.* The values in this table are the Curie and Weiss constants obtained after the mass susceptibilities were corrected for volume expansion, the coefficient of volume expansion being assumed as 10^{-4} per degree centigrade for all the crystals.

Crystal	Δ	Δ_2	Δ_3	C_{m1}	C_{m2}	C_{m3}
$Co(NH_4)_2(SO_4)_26H_2O$	−44	93	0	3.05	3.4	3.1
$CoK_2(SO_4)_26H_2O$	15	100	78	3.6	3.6	3.5
$CoSO_47H_2O$	31	55	56	3.4	3.0	3.3
$Ni(NH_4)_2(SO_4)_26H_2O$	40	35	35	1.47	1.40	1.40
$Cu(NH_4)_2(SO_4)_26H_2O$	−1	33	6	0.49	0.465	0.485
$CuK_2(SO_4)_26H_2O$	23	30	27	0.525	0.435	0.505

TABLE IV. *Susceptibilities of powdered crystals.* In this table χ is the mass susceptibility, and χ_m' the molecular susceptibility corrected for diamagnetism. C_m and Δ are the Curie and Weiss constants, respectively. Temperatures are in degrees centigrade.

Crystal Powder	T	$\chi\times10^6$	$\chi_m'\times10^6$
$Co(NH_4)_2(SO_4)_26H_2O$	56	23.2	9340
$C_m=3.2$	22	25.9	10400
$\Delta=14$	−7	28.8	11560
$CoK_2(SO_4)_26H_2O$	55	21.3	9490
$C_m=3.45$	19	23.8	10580
$\Delta=37$	−38	28.5	12600
$CoSO_47H_2O$	45	30.7	9030
$C_m=3.4$	19	34.3	9780
$\Delta=60$	−20	38.3	10880
$Ni(NH_4)_2(SO_4)_26H_2O$	52	9.60	3960
$C_m=1.38$	20	10.55	4350
$\Delta=27$	−40	13.08	5340
$Cu(NH_4)_2(SO_4)_26H_2O$	56	3.00	1380
$C_m=0.47$	20	3.42	1550
$\Delta=15$	−39	4.25	1890
$CuK_2(SO_4)_26H_2O$	56	2.68	1363
$C_m=0.46$	20	3.06	1538
$\Delta=13$	−40	3.86	1888

with the average mass susceptibilities of the crystals. In general there is no appreciable consistent difference of the sort which might be expected if the correction for volume expansion were of importance.

In Table IV are given the results of the measurements on the powdered crystals. These were not originally intended as precision measurements, and as has already been pointed out under the heading *Crystals*, they are probably somewhat less accurate than the results of Table I. The agreement between the powder measurements and the averages for the crystals is in general so good, however, as to warrant their inclusion as a check on the latter.

DISCUSSION

Comparison of the results obtained at room temperatures by Fincke, Jackson, Rabi, and the writer is given in Table V. The agreement between the two latter is in general within the experimental error, except for the crystals containing copper, where there is a consistent difference of from 2 to 4

TABLE V. *Comparison of results.* This table contains a comparison of the results of different investigators at room temperatures reduced to the common temperature 27°C. The K's are the principal volume susceptibilities, and θ is the angle between K_1 and the c crystallographic axis.

Investigator	$K_1 \times 10^6$	$K_2 \times 10^6$	$K_3 \times 10^6$	θ
		$Co(NH_4)_2(SO_4)_2 6H_2O$		
Bartlett	56.8	40.6	49.3	−43
Fincke*	55.9	43.6	45.5	−27
Jackson	48.0	40.4	46.9	−31
Rabi	56.2	40.7	48.9	−44**
		$CoK_2(SO_4)_2 6H_2O$		
Bartlett	57.3	43.9	47.6	−13
Fincke*	66.6	49.6	77.2	−21
Jackson	61.1	49.6	53.6	−20
Rabi	57.6	44.6	48.6	−13**
		$CoSO_4 7H_2O$		
Bartlet	70.4	58.2	62.6	−55
Fincke*	70.9	64.0	68.5	−40
		$Ni(NH_4)_2(SO_4)_2 6H_2O$		
Bartlett	20.2	19.7	19.7	−17
Fincke*	19.6	15.8	18.0	−16
Rabi	20.2	19.9	20.0	−17**
		$Cu(NH_4)_2(SO_4)_2 6H_2O$		
Bartlett	7.08	5.65	6.83	−79
Rabi	6.80	5.40	6.62	−74
		$CuK_2(SO_4)_2 6H_2O$		
Bartlett	7.14	5.80	6.98	−102
Rabi	7.52	5.62	6.83	−99

* Fincke does not state the temperature at which his measurements were made.

** There is a misprint in the published values of θ in Rabi's paper. The values given for cobalt ammonium and cobalt potassium sulphate should be interchanged, as should those for nickel ammonium and nickel potassium.

percent. This difference may be partially explained by an indeterminate temperature correction, as Rabi's measurements were not primarily concerned with temperature, which accordingly was not determined with care. There remains a discrepancy in the value of K_1 for copper potassium sulphate which is not consistent with the other differences. Comparing the values of the copper group with those of the nickel and cobalt groups in Rabi's paper, it appears that the value given in this paper is more consistent than that given by Rabi. In general Fincke's and Jackson's results do not agree nearly so closely, either with each other or with Rabi.

Comparison of the Curie and Weiss constants found for the cobalt double sulphates by Jackson and by the writer shows qualitative agreement for the Weiss constants, and reasonably good quantitative agreement for the Curie constants, considering the accuracy of the determinations. For the Curie constants this is of the order of 3 percent, and for the Weiss constants not better than 5°. Jackson's value for the maximum principal susceptibility of cobalt ammonium sulphate is inconsistent with the relative values bound by the other three investigators of this salt. Agreement between the average values of the constants in this paper and those found by Jackson for the cobalt and nickel double sulphates in powdered form is qualitatively good. In the case of the curves in this paper for nickel ammonium sulphate, the writer has drawn them as straight lines. An equally good case might be made for drawing them with a slight downward curvature at the lower end. Further data at still lower temperatures are needed to indicate which is nearer the truth.

The effect of changing the alkali ion from ammonium to potassium seems to be to increase slightly the Curie constants, and to make the Weiss constants more positive. There appear to be definite, though small, differences in the Curie constants for different axes of the same crystal in some cases. A recent note by Jordahl, Penney, and Schlapp[6] states that this may be expected from theoretical considerations.

Thus far most of the work done on this problem has been done over a comparatively small range of temperatures near room temperature, or at very low temperatures. The first type is open to the objection that the range of temperature is scarcely sufficient to give high accuracy to the determination of the constants, while the second has the difficulty that at low temperatures the variation from the Weiss law makes computation of the constants somewhat uncertain. Thus in certain of Jackson's work no values of susceptibilities are available between room temperature and about 75°K, at which point deviation from the Weiss law is already taking place. A complete run upon a typical crystal like cobalt ammonium sulphate from room temperature or above down to the lowest temperatures obtainable, with points at frequent temperature intervals, seems needed as an adequate test of theory.

Any theoretical discussion of the magnetic behavior of these crystals must recognize that in the case of the copper group the diamagnetic correction is particularly important, a small uncertainty having a considerable effect on the constants. It is quite probable from results on diamagnetic crystals[4,11]

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[11] W. Voigt and S. Kinoshita, Ann. d. Physik [4] **24**, 492 (1907).

that this correction should be different in different directions. At present it is practically impossible to obtain from susceptibility measurements an accurate knowledge of what the paramagnetic susceptibilities of this group really are. The thermal expansion is in all likelihood different along different axes, and consequently the force field acting on the paramagnetic ion will be changed in both magnitude and direction. That this may be the case is shown by the particular example of copper ammonium sulphate, where the ellipsoid of induction is rotated almost 15 degrees with respect to the crystallographic axes over a temperature range of 95 degrees. This type of datum may serve to give insight into the nature of these force fields and their dependence on temperature. An investigation of triclinic crystals, where there are no necessary fixed relations between crystal axes and ellipsoid of induction, might yield results of interest.

In conclusion the writer wishes to express his appreciation of the interest and advice of Professor I. I. Rabi, who suggested this problem to him, and his thanks to Professor N. C. Little for placing at his disposal the magnet used for measuring the susceptibilities of the solutions.