Magnetic Susceptibilities of Salts of the Iron Group Elements

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Measurements of the paramagnetic susceptibilities of powdered crystals of several salts of the iron group elements have been made over the temperature range 80° to 300°K. The results are in good agreement with the theoretical predictions of Van Vleck and his co-workers in the cases where the theory is applicable. Several of the nickel and cobalt complex salts have susceptibilities which vary in an unusual manner with the temperature.

In most of the salts of the iron group elements, the metallic ion belonging to this group has an outermost incomplete shell of $3d$ electrons. When free the metallic ion shoud have a magnetic moment corresponding to the total angular momentum of the $3d$ electrons. However, the crystalline fields due to the groups surrounding the metallic ion in the salt act on this ion and largely destroy the orbital contribution of the ion's electrons to the magnetic moment,[1] leaving a magnetic moment which corresponds fairly closely to the resultant spin momentum of the electrons. If the magnetic moment is due to spin only the ion should be magnetically isotropic with a paramagnetic susceptibility per mole given by the Bose-Stoner expression

$$\chi = N\beta^2 4S(S+1)/3kT, \qquad (1)$$

where S is the resultant spin quantum number, N is Avogadro's number and β is the Bohr magneton. However, the orbital angular momentum is not entirely destroyed, the remnants giving rise to the magnetic anisotropy and deviations from (1) that are observed.

Assuming a crystalline field possessing only rhombic symmetry but with the deviations from cubic symmetry small, Van Vleck[2] has shown that Ni^{++} and Cr^{+++} should be nearly magnetically isotropic and should have mean susceptibilities that deviate only slightly from (1). Co^{++}, however, should show a larger anisotropy and larger deviations from (1). Cu^{++} resembles Ni^{++} and Cr^{+++} but here other factors complicate the situation. Using a complicated perturbation technique and neglecting the effect of the rhombic field, Penney and Schlapp[3] were able to find a simple expression for the mean molar susceptibilities of Ni^{++} and Cr^{+++} which included the coefficient D. No simple formula could be set up for the mean susceptibility of Co^{++}. However Jordahl[4] was able to find a simple expression for Cu^{++}. Penney and Schlapp and Jordahl found that in the case of several Ni^{++}, Cr^{+++} and Cu^{++} hydrated salts, when the experimental value of the mean susceptibility at one temperature is used to find the value of D, the expressions fit very well the experimental data for the other temperatures. The sign of D is found to be positive in all cases. Gorter[5] has shown that the positive sign corresponds to six groups or atoms arranged at the corners of an octahedron around the metallic ion. Thus the results of the calculations give a clue to the arrangement of the groups around the metallic ion in the salt molecule. X-ray investigations, in the cases that they have been carried out, lead to the same arrangement.

The writer has extended the experimental data to other Cr^{+++}, Ni^{++}, Co^{++} and Cu^{++} salts. Powdered crystals of these salts were used throughout. The salts were all carefully purified and analyzed. To determine the susceptibilities of the specimens the Gouy method of weighing a rod of the specimen with and without a magnetic field at right angles to the bottom of the rod was adopted. The magnetic field strength of about 6000 gauss, was held constant by controlling both the temperature of the magnet and the current through its coils. The absolute susceptibilities of the salts were determined by calibrating the rods with an aqueous solution of nickel chloride. The error in the measurement of the relative susceptibilities of the salts at different temperatures was at the most 0.3 percent, but due to the difficulty

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[1] For a general discussion see Van Vleck, *Theory of Electric and Magnetic Susceptibilities*.

[2] Van Vleck, Phys. Rev. **41**, 208 (1932).

[3] Penney and Schlapp, Phys. Rev. **42**, 666 (1932).

[4] Jordahl, Phys. Rev. **45**, 87 (1933).

[5] Gorter, Phys. Rev. **42**, 437 (1932).

of determining the correction for apparent densities of the powders when packed into the rods and the inaccuracy in the correction for diamagnetism, the error in the measurement of the absolute susceptibilities was probably about $\frac{1}{2}$ to 1 percent. The susceptibilities were determined at six temperatures, the highest being room temperature and the lowest that of liquid air. For the intermediate temperatures a condenser reflux system, which used liquid air to cool the condenser reflux and ethylene and propane as the gases which were condensed, was built. These condensed gases, boiling under constant pressure, maintained a constant temperature in the bath surrounding the specimen. Propane boiling under atmospheric pressure gave a temperature of about -40°C. By reducing the pressure a temperature of about -70°C could be obtained. Likewise ethylene gave bath temperatures of about -110° and -135°C. The temperature of the test body itself, as measured by thermocouples, could be held constant to about 0.2°C.

Summary and Discussion of Results

Chromium^{+++}

The simple expression for the mean molar susceptibility of the Cr^{+++} ion derived by Penney and Schlapp is

$$\chi=(15N\beta^2/3kT)(1-2\lambda/5D)^2, \qquad (2)$$

where λ is the constant of the orbit-spin interaction. This expression is in good agreement with the Leyden data for the mean susceptibility of chrome alum. Using $\lambda=87$ cm^{-1}, Penney and Schlapp find $D=3730$ cm^{-1} for this salt.

The writer's data for $K_3Cr(SCN)_6\cdot 4H_2O$ are given in Table I. Here κ is the susceptibility per gram of the salt. Since κT is constant within experimental error the data are in good agreement with (2). Using $\kappa T=30.10\cdot 10^{-4}$ a value of $D=1480$ cm^{-1} is obtained. A second run gave an average value of $\kappa T=30.30\cdot 10^{-4}$. With this value $D=1720$ cm^{-1}. This shows that, as Penney and Schlapp have pointed out, too much reliance should not be placed on the numerical value of D. However, the difference between the D for this compound and that found for chrome alum is too large to be accounted for by experimental error, and can be regarded as a rough measure of the differences of the cubic fields in the two compounds.

TABLE I. *Susceptibility per gram of $K_3Cr(SCN)_6\cdot 4H_2O$.* A diamagnetic correction of 0.44 per gram has been applied.

$\kappa\cdot 10^6$	10.19	13.07	14.59	17.82	20.31	36.64
T°K	295.2	230.7	206.6	169.0	148.5	82.0
$\kappa T\cdot 10^4$	30.08	30.15	30.14	30.12	30.16	30.05

Nickel^{++}

In this case Penney and Schlapp obtain for the mean molar susceptibility an expression

$$\chi=(8N\beta^2/3kT)(1-4\lambda/5D)+4N\beta^2/5D. \qquad (3)$$

The Leyden data for $NiSO_4\cdot 7H_2O$ are in good agreement with (3) except for the points at liquid hydrogen temperatures. Even at these temperatures the disagreement is not serious. Using $\lambda=-335$ cm^{-1}, Penney and Schlapp obtain $D=1485$ cm^{-1}. There is, however, a numerical error in their calculation. D should be 1103 cm^{-1}. The writer's data for several nickel salts are given in Tables II, III, IV and V and Figs. 1 and 2.

If we use $\kappa T=47.30\cdot 10^{-4}$ for $NiSO_4\cdot 6H_2O$ (Table II) at 169°K we get a value of $D=1208$ cm^{-1}. Eq. (3) then fits the experimental data very well as is shown in Fig. 1. The value of D for this

TABLE II. *Susceptibility per gram of $NiSO_4\cdot 6H_2O$.* The diamagnetic correction used was 0.42 per gram. (See Fig. 1.)

$\kappa\cdot 10^6$	16.13	20.78	23.19	27.96	56.89
T°K	298.5	230.1	205.3	169.0	82.2
$\kappa T\cdot 10^4$	48.14	47.81	47.61	47.25	46.76

TABLE III. *Susceptibility per gram of $Ni(NO_3)_2\cdot 6H_2O$.* The diamagnetic correction used was 0.37 per gram. (See Fig. 1.)

$\kappa\cdot 10^6$	15.14	19.10	21.28	25.78	29.03	51.73
T°K	293.5	230.0	205.6	169.0	149.3	83.0
$\kappa T\cdot 10^4$	44.43	43.93	43.76	43.58	43.34	42.93

TABLE IV. *Susceptibility per gram of $Ni(NO)_2\cdot 4NH_3$.* The diamagnetic correction used was 0.39 per gram. (See Fig. 1.)

$\kappa\cdot 10^6$	18.79	23.57	26.57	31.53	63.23
T°K	293.8	231.0	203.1	169.0	82.6
$\kappa T\cdot 10^4$	55.20	54.45	53.97	53.29	52.23

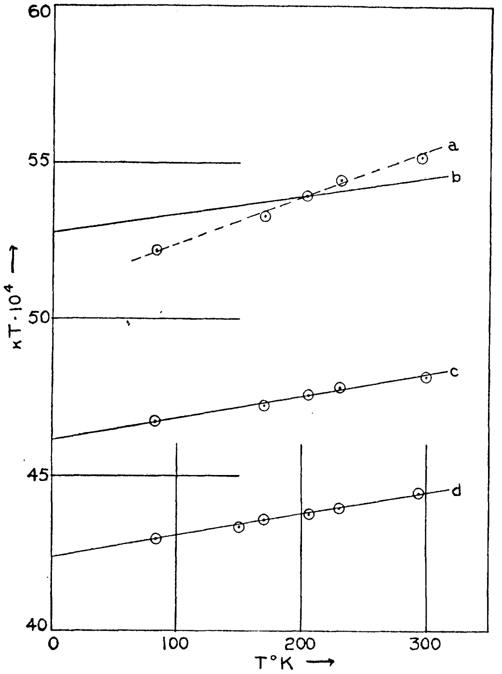

FIG. 1. *a*, the experimental curve for $Ni(NO_2)_2 \cdot 4NH_3$; *b*, the theoretical curve for $Ni(NO_2)_2 \cdot 4NH_3$; *c*, the theoretical curve for $NiSO_4 \cdot 6H_2O$; *d*, the theoretical curve for $Ni(NO_3)_2 \cdot 6H_2O$; the circles in all cases, represent experimental values of $\kappa T \cdot 10^4$.

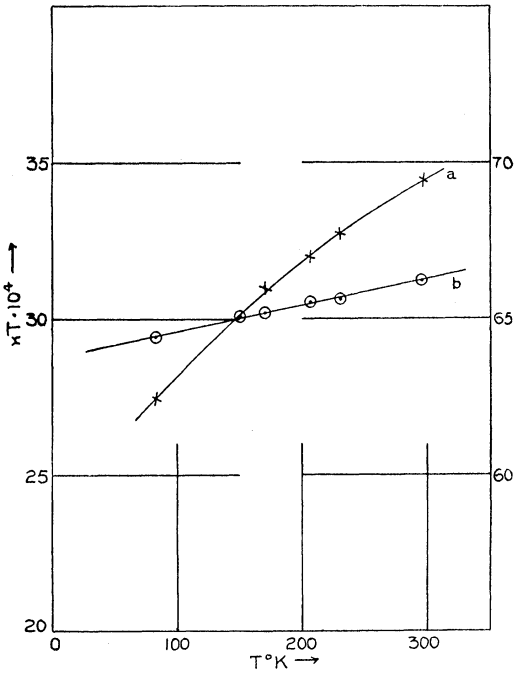

FIG. 2. *a*, experimental curve for $K_2(SCN)_4 \cdot 4H_2O$ (see ordinate scale on right); *b*, experimental curve for $Ni(CN)_2 \cdot C_6H_6 \cdot NH_3$ (see ordinate scale on left).

salt is the same within experimental error as the value for $NiSO_4 \cdot 7H_2O$, showing that the crystalline fields are very similar in the two compounds. This is to be expected because of the similarity of the two salts.

If we use $\kappa T = 43.58 \cdot 10^{-4}$ for $Ni(NO_3)_2 \cdot 6H_2O$ (Table III) at 169°K we get a value of $D = 1106$ cm^{-1}. Eq. (3) is then in good agreement with the experimental results as Fig. 1 shows. The values of the susceptibilities of a second sample fall on a line having the same slope as that of sample one, but the absolute value of the susceptibility is somewhat different. Using the κT value for the second sample at 169°K which is $= 43.95 \cdot 10^{-4}$ we find a value of $D = 1064$ cm^{-1}. The results show that the nitrate has a cubic field closely resembling that of the sulphates. The rhombic fields in the three salts must be of the same order also, for although the presence of a comparatively small rhombic field will not materially change the slope of the theoretical curve given by (3) it will change the value of D necessary to get agreement.

TABLE V. *Susceptibility per gram of* $Ni(CN)_2 \cdot C_6H_6 \cdot NH_3$. The diamagnetic correction used was 0.43 per gram. (See Fig. 2.)

$\kappa \cdot 10^6$	10.56	13.33	14.87	17.87	20.15	35.64
T°K	296.0	230.0	205.5	169.0	149.3	82.5
$\kappa T \cdot 10^4$	31.26	30.66	30.55	30.20	30.09	29.40

Using the experimental value of $\kappa T = 53.97 \cdot 10^{-4}$ for $Ni(NO)_2 \cdot 4NH_3$ (Table IV) at 203.1°K in (3), one obtains $D = 1650$ cm^{-1}. However, as Fig. 1 shows, the theoretical curve does not fit the experimental points at all, and widely different values of D would be secured if values of κT corresponding to other values of the temperature were used. Under these conditions it is hard to predict the type of crystalline field existing in the salt. The salt may have a predominantly rhombic field in which case (3) will not hold, or it may have a predominantly cubic one but with a negative D, in which case (3) will again not hold. The second choice corresponds to a field due to four groups arranged on the corners of a tetrahedron around the metallic ion.[5] Neither choice, however, offers a unique solution. The Bohr magneton number $= 3.12$ at room temperature is above the spin only value of 2.83.

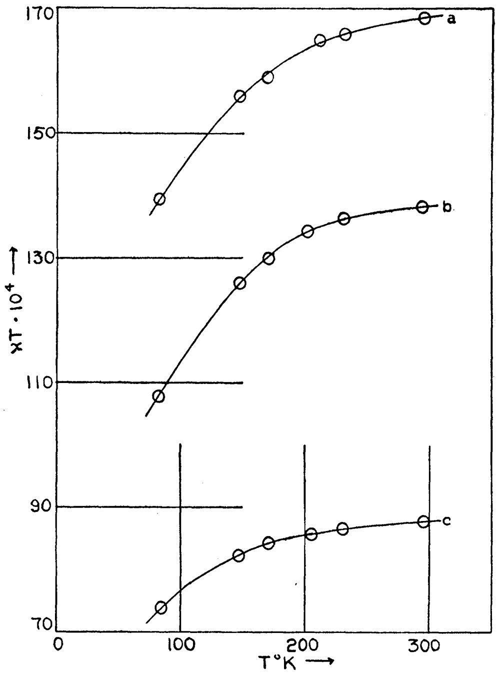

FIG. 3. *a*, experimental curve for $CoSO_4 \cdot 6NH_3$; *b*, experimental curve for $CoCl_2 \cdot 6NH_3$; *c*, experimental curve for $Co(CN)_2 \cdot 2H_2O$.

For $Ni(CN)_2 \cdot C_6H_6 \cdot NH_3$ (Table V) there is no possibility of (3) agreeing with the experimental data. The Bohr magneton number at 300.6°K = 2.27 is below the spin only value. Under these conditions D would be negative and (3) would not be valid. To explain this one could assume that there is a predominantly rhombic or perhaps axial field, which quenches not only the orbital but also part of the spin contribution to the magnetic moment, present in the salt. This case resembles that of $K_2Ni(CN)_4 \cdot H_2O$. This salt has been found to be diamagnetic, and as Pauling has shown,[6] it probably has a predominantly tetrahedral field, which destroys the magnetic moment entirely. The writer has checked the experimental data for this salt, and also finds it to have a diamagnetic susceptibility which is independent of the temperature used.

The Bohr magneton number for NiO (Table VI) at 297.3°K is 1.27. This is far below the spin only value. However, in this salt the "magnetic dilution" is small and exchange forces come in. This case is too difficult to handle theoretically.

TABLE VI. *Susceptibility per gram of NiO.* The diamagnetic correction used was 0.6 per gram.

$\kappa \cdot 10^6$	9.05	8.60	8.46	8.26
T°K	297.3	230.0	199.7	82.3

As Table VI shows, the susceptibility, in contrast to that of other nickel salts, actually decreases with decreasing temperature.

Cobalt^{++}

Here the situation is much more complicated than it is for the other three ions. In Co^{++} a multiplet level lies lowest and as the temperature changes the electron population of each level of the multiplet changes. As the individual levels each contribute a different amount to the susceptibility, we should expect a dependence of the susceptibility on the temperature different from that in the other ions where a singlet level is the lowest. This will be true even if the crystalline field is of the same type considered in these other ions, that is cubic with a positive D.

The Bohr magneton number for $K_2Co(SCN)_4 \cdot 4H_2O$ (Table VII) at 296.8°K is 4.96. The variation of κT with T resembles that found for the cobalt hydrates which have six water molecules around the metallic ion at the corners of an octahedron. The Bohr magneton number, however, is slightly lower. This compound thus apparently had a predominant cubic crystalline field like those of the hydrates mentioned, although in this case it is impossible to say just what groups surround the metallic ion. Since the Bohr magneton number is closer to the spin only value, the rhombic field is probably larger in this salt. If the metallic ion is surrounded by four groups at the corners of a tetrahedron the sign of D should change,[5] and Co^{++} should then resemble Ni^{++}.[2] The data indicate that such a configuration is probably not present in this salt, as the observed deviations from Curie's law are too large.

TABLE VII. *Susceptibility per gram of* $K_2Co(SCN)_4 \cdot 4H_2O$. The diamagnetic correction used was 0.44 per gram. (See Fig. 2.)

$\kappa \cdot 10^6$	23.39	29.38	32.43	39.08	75.69
T°K	296.8	230.3	206.5	169.0	82.5
$\kappa T \cdot 10^4$	69.42	67.66	66.96	66.00	62.43

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[6] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

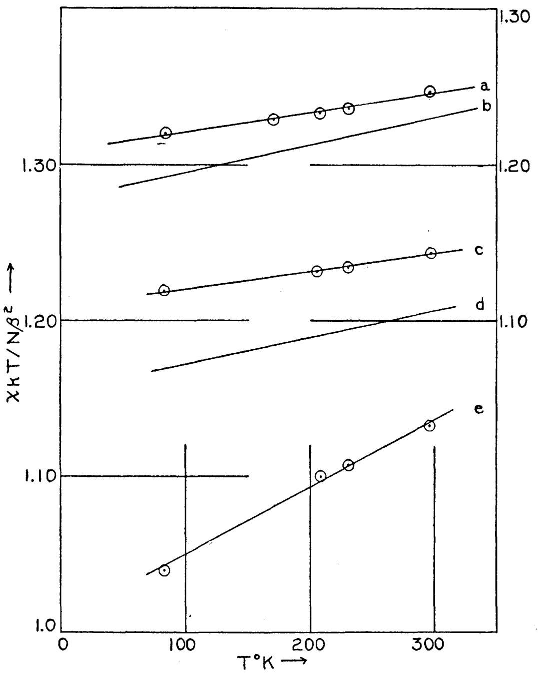

FIG. 4. *a*, experimental curve for $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (see ordinate scale on right); *b*, Jordahl's theoretical curve for $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (see ordinate scale on right); *c*, experimental curve for $CuK_2(SO_4)_2 \cdot 6H_2O$ (see ordinate scale on left); *d*, Jordahl's theoretical curve for $CuK_2(SO_4)_2 \cdot 6H_2O$ (see ordinate scale on left); *e*, experimental curve for $CuSO_4 \cdot 4NH_3 \cdot H_2O$ (see ordinate scale on left).

The Bohr magneton for $CoCl_2 \cdot 6NH_3$ (Table VIII) at 292.9°K is 5.09. Although from its composition the crystalline field of this salt should resemble the fields of the hydrates spoken of above, Fig. 4 shows that the variation of κT with T is altogether different. At higher temperatures the curve tends to flatten out so as to give a variation resembling that of the hydrates. Also at room temperatures the Bohr magneton number is of the same order as that of the hydrates. At lower temperatures, however, the value of κT for this salt drops much faster than in the case of the hydrates indicating that the contribution to the susceptibilities of the lower levels of the multiplet is for this salt much smaller, probably going below the spin only values at temperatures below that of liquid air. Possibly at still lower temperatures, when the electrons are largely in the lower levels, the curve will tend to flatten out again at a much lower value of κT. If we had plotted the ordinary curve of the experimentalists, where $1/\kappa$ is plotted against T, we should find that the higher temperature points lie on a straight line and that the lower temperature points lie on another straight line which has quite a different slope. This would seem to indicate a sharp change of some sort inside the crystal at a certain temperature, which is not shown by the κT curve. This second procedure is very artificial and has no real theoretical significance.

TABLE VIII. *Susceptibility per gram of* $CoCl_2 \cdot 6NH_3$. A diamagnetic correction of 0.54 per gram was used. (See Fig. 3.)

$\kappa \cdot 10^6$	47.23	59.11	66.90	77.00	85.11	131.4
T°K	292.9	231.0	200.7	169.0	148.3	82.1
$\kappa T \cdot 10^4$	138.3	136.5	134.3	130.1	126.0	107.8

The Bohr magneton number for $CoSO_4 \cdot 6NH_3$ (Table IX) at 294.2°K is 5.91. The variation of κT with T resembles that for $CoCl_2 \cdot 6NH_3$. However, at room temperature the Bohr magneton number is higher than in the case of the chloride. This merely means that the susceptibility in the upper levels is not destroyed as much. Such a large value of the Bohr magneton number at room temperature is unusual, however. The lower levels are greatly affected as in the case of the chloride. The crystalline fields are probably a great deal alike in the two cases.

TABLE IX. *Susceptibility per gram of* $CoSO_4 \cdot 6NH_3$. The diamagnetic correction used was 0.47 per gram. (See Fig. 3.)

$\kappa \cdot 10^6$	57.26	71.72	78.37	93.90	105.1	169.1
T°K	294.2	231.3	210.3	169.2	148.3	82.4
$\kappa T \cdot 10^4$	168.5	165.8	164.8	158.9	155.8	139.4

The Bohr magneton number for $Co(CN)_2 \cdot 2H_2O$ (Table X) at 294.5°K is 3.27 while the spin only value is 3.87. In this case the Bohr magneton number at room temperature is much smaller than in the preceding two cases. However, the slope of the κT curve at room temperature is about the same as that of the preceding two cobalt salts. Also, as in the case of the other two

TABLE X. *Susceptibility per gram of* $Co(CN)_2 \cdot 2H_2O$. A diamagnetic correction of 0.32 per gram has been used. (See Fig. 3.)

$\kappa \cdot 10^6$	29.77	37.60	42.02	49.80	55.00	88.93
T°K	294.5	229.7	203.7	169.0	149.3	83.0
$\kappa T \cdot 10^4$	87.68	86.36	85.61	84.16	82.13	73.80

salts, a rapid drop of κT is found at the lower temperatures.

Copper^{++}

Jordahl[4] has found an expression for the principal susceptibilities of Cu^{++} salts which he has applied to Bartlett's[7] data for $Cu(NH_4)_2(SO)_2 \cdot 6H_2O$ and $CuK_2(SO_4)_2 \cdot 6H_2O$. By proper choice of parameters fair agreement can be secured between this expression and the experimental results. However, Bartlett's data are limited to a small range of temperatures around room temperature. The writer has extended the data for the mean susceptibility to lower temperatures in order to check the expression of Jordahl for the mean at these temperatures. This, of course, gives somewhat of a check on the expression for the principal susceptibilities.

In the work on Cu^{++} (Table XI) the author has plotted $\chi kT/N\beta^2$ instead of κT. If the Cu^{++} ion has the spin only value of 1.73 Bohr magnetons the expression $\chi kT/N\beta^2 = 1$. The diamagnetic correction of 0.45 per gram which was applied to $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (Table XI) is the same value that Bartlett used. A second sample had susceptibilities lying on a line with the same slope as that of sample one, but the value of $\chi kT/N\beta^2 =$ 1.240 at 296.1° was somewhat lower. Jordahl's theoretical curve drawn in accordance with Bartlett's data is also shown in Fig. 4. The agreement between this curve and the writer's data is only fair. This is to be expected as Bartlett's range of temperature was too small to establish the slope accurately and the absolute values cannot be expected to check much better than to about 1 percent. By using the cubic expression for Cu^{++} with a value of $D = 17{,}200$ cm^{-1}, quite good agreement can be secured with the author's data. Of course the more complete expression given by Jordahl could be used but no satisfactory values of the parameters involved in it can be obtained from a knowledge of the mean susceptibilities only. It might be noted, however, that the values of these parameters obtained from Bartlett's data on the principal susceptibilities would have to be changed somewhat in order to be in accordance with the writer's data.

TABLE XI. *Susceptibility per gram of* $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$. A diamagnetic correction of 0.45 per gram was used. (See Fig. 4.)

$\kappa \cdot 10^6$	3.927	5.009	5.544	6.770	13.640
T°K	295.7	229.8	207.0	169.0	83.3
$\chi kT/N\beta^2$	1.247	1.236	1.233	1.229	1.220

The results for $CuK_2(SO_4)_2 \cdot 6H_2O$ (Table XII) are not in as good agreement with Bartlett's results as they were for the preceding one. The slope agrees fairly well but the writer's absolute values are about 3 percent higher. In fact the values of $\chi kT/N\beta^2$ found by the author agree very well with his values for $Cu(NH_4)_2(SO_4) \cdot 6H_2O$. This means that the cubic expression with $D = 17{,}200$ cm^{-1} will also give good agreement with the data for $CuK_2(SO_4)_2 \cdot 6H_2O$. This is not unexpected as the same thing was found in the case of Ni^{++}. A value of D of the same order will also fit the Leyden data for $Cu(SO_4) \cdot 5H_2O$[4]. It might be noted that if Bartlett's values for $CuK_2(SO_4) \cdot 6H_2O$ were all shifted up by a constant amount good agreement would be secured with the writer's data.

TABLE XII. *Susceptibility per gram of* $CuK_2(SO_4)_2 \cdot 6H_2O$. The diamagnetic correction used was 0.41 per gram. (See Fig. 4.)

$\kappa \cdot 10^6$	3.541	4.514	5.048	12.51
T°K	296.8	230.2	205.6	82.1
$\chi kT/N\beta^2$	1.243	1.234	1.232	1.219

The susceptibilities of $CuSO_4 \cdot 4NH_3 \cdot H_2O$ (Table XIII) are quite different from those in the other cases suggesting that the field is different. Without data for the principal susceptibilities no satisfactory choice of the field can be made.

TABLE XIII. *Susceptibility per gram of* $CuSO_4 \cdot 4NH_3 \cdot H_2O$. A diamagnetic correction of 0.42 per gram was used. (See Fig. 4.)

$\kappa \cdot 10^6$	5.81	7.28	8.06	19.22
T°K	295.0	230.2	206.7	81.9
$\chi kT/N\beta^2$	1.132	1.107	1.100	1.039

The writer wishes to express his thanks to Professor J. H. Van Vleck for continued interest in this work and to Professor C. E. Mendenhall for many helpful suggestions in the experimental arrangements.

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[7] B. W. Bartlett, Phys. Rev. **41**, 818 (1932).