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The Antiferromagnetism of Anhydrous Sulfates of Ni^{++}, Fe^{++}, Co^{++} and Cu^{++}

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The temperature dependence of magnetic susceptibility has been studied in the temperature range 12 to 300° K, for the four anhydrous sulfates $NiSO_4$, $FeSO_4$, $CoSO_4$ and $CuSO_4$. For the first three sulfates, the susceptibility maximum characteristic of an antiferromagnetic transition was observed. It is hypothesized that in $CuSO_4$ at 35° K, half the Cu^{++} ions form an antiferromagnetic array. It is shown that the magnetic susceptibility of $NiSO_4$, below the Curie point, decreases with temperature according to a quadratic law.

1. INTRODUCTION

ANTIFERROMAGNETISM was first predicted theoretically by Landau[1] and was observed experimentally by Shubnikov and Trapeznikova[2] and by Shalyt[3] in the special case of a layered ordering in the compounds $FeCl_2$, $CoCl_2$ and $NiCl_2$. In the ensuing years a considerable number of chemical compounds of the iron group, showing characteristic ferromagnetic properties, were studied (see, for example, the review by Nagamiya, Yosida and Kubo[4]). The chief shortcoming of most of these studies was that the experimental data obtained in them were insufficient for establishing the temperature dependence of the magnetic susceptibility below the Curie point.

In the present study, the magnetic properties of anhydrous sulfates of nickel, iron, cobalt and copper were investigated. X-ray analysis[5] of these compounds shows that in them the shortest distance between magnetic ions is less than 5 A. This provided grounds for expecting antiferromagnetism to exist at liquid hydrogen temperatures. However, results obtained in 1924 by Jackson[6] on the magnetic susceptibility of $NiSO_4$, $FeSO_4$ and $CoSO_4$ at hydrogen and nitrogen temperatures were insufficient for drawing any conclusions in regard to an antiferromagnetic transition in these compounds.

2. APPARATUS AND SPECIMENS

The magnetic susceptibility was measured by the Faraday method, with apparatus developed earlier by Borovik-Romanov and Kreines[7]. This apparatus permitted continuous coverage of the broad temperature range from 12 to 300° K. The temperature was measured with a copper-constantan thermocouple, calibrated against a standard resistance thermometer[8]. The error of measurement at hydrogen temperatures was not over ±0.5° C; with increasing temperature it decreased to ±0.1°. The susceptibility measurement was made at several values of field intensity from 500 to 2500 Oe (oersteds). The error in the absolute determination of the susceptibility was not over ±5%, and in the relative determination less than ±2%. No correction was made for the diamagnetism of $SO_4^=$, since it amounted to less than 1%.

All the specimens of anhydrous sulfates that were studied were obtained by dehydration of the corresponding crystalline hydrates. The original products used were of "ch. d. a" make. An anhydrous sample of $NiSO_4$ was obtained by calcination of the heptahydrate at a temperature of about 500° C for two to three hours. Observations were also made on a sample dehydrated by melting of $NiSO_4 \cdot 7H_2O$ in ammonium sulfate and subsequent evaporation of the melt[9]. In both cases the sample was obtained in the form of a fine-grained yellow powder.

The anhydrous sample of $FeSO_4$ was made by heating the heptahydrate in a stream of pure dry hydrogen at about 300° C for four hours. A sample obtained in this way could contain up to 3% $Fe_2(SO_4)_3$. The anhydrous sample of $CoSO_4$ was obtained by heating $CoSO_4 \cdot 7H_2O$ for five hours at 500° C. The results presented below relate to this sample, which had the form of a pale violet powder. Another sample was also studied; it was obtained by evaporation of a solution of $CoSO_4 \cdot 7H_2O$ in concentrated sulfuric acid[10]. By this method fine violet crystals were obtained. Upon cooling, these crystals crumble into a powder and lose their bright color. The magnetic properties of this powder differ from the magnetic properties of $CoSO_4$ obtained by calcination. This is of course connected with the fact that crystals obtained by evaporation from a solution contain a certain amount of H_2SO_4.

The anhydrous $CuSO_4$ was obtained in the form of a white powder by heating of blue vitriol to 300° C with constant stirring over a period of two hours.

TABLE I

Author	$\chi_M \cdot 10^3$		
	$NiSO_4$	$FeSO_4$	$CoSO_4$
Jackson[6]	4.13	10.3	9.63
Present work	4.97	12.4	9.87

3. RESULTS OF THE MEASUREMENTS

The magnetic susceptibility of all four anhydrous sulfates was measured at temperatures from 13 to 300° K. Table I shows the values obtained by us for the molar magnetic susceptibility of the three sulfates $NiSO_4$, $FeSO_4$ and $CoSO_4$ at room temperature ($T = 290°$ K). The magnetic susceptibility of these sulfates was studied earlier by Jackson[6], whose data are also shown in Table I. The low values obtained by Jackson can be attributed to incomplete dehydration of the samples studied by him.

Figure 1 shows the temperature dependence of the molar magnetic susceptibility of the three sulfates. In all of them one observes the characteristic maximum of the susceptibility at Curie temperatures $T_C = 37°$ K for $NiSO_4$, 21° K for $FeSO_4$ and 15.5° K for $CoSO_4$. In Jackson's work, measurements were made only in baths of liquid hydrogen and liquid nitrogen; consequently, he was unable to detect these maxima. At temperatures appreciably higher than T_C, the Curie-Weiss law

$$\chi = C/(T + \Theta) \qquad (1)$$

is obeyed by all four sulfates, with the values of the constants C and Θ listed in Table II.

The results obtained for the anhydrous sample of $CuSO_4$ are shown in Fig. 2. The magnetic susceptibility of this compound was measured earlier in the Leiden laboratory, but likewise only in baths of liquid hydrogen and nitrogen. Those results, also, are shown in Fig. 2. The chief difference is observed at temperatures below 20° K, where, according to our measurements, the susceptibility noticeably increases, but according to the data of the Leiden laboratory it depends little on temperature. This is perhaps attributable to insufficient heat exchange between the bath and the specimen in the apparatus used in the Leiden laboratory. In agreement with the results of the Leiden laboratory, we observed a slight dependence of the susceptibility on the field at hydrogen temperatures. Upon change of the magnetic field from 1800 to 4500 Oe, the susceptibility decreased 10%. Note the abrupt break in the curve in the neighborhood of 35° K.

TABLE II

Compound	Range of validity of Curie-Weiss law T in °K	C_M	Θ
$NiSO_4$	45—300	1.83	82
$FeSO_4$	40—300	3.98	30.5
$CoSO_4$	95—300	3.37	47
$CuSO_4$	40—300	0.45	55

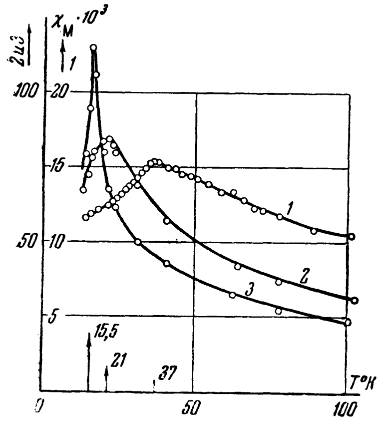

FIG. 1. Temperature dependence of the molar magnetic susceptibility χ_M of anhydrous sulfates: *1*, $NiSO_4$; *2*, $FeSO_4$; *3*, $CoSO_4$. The values of T_C are shown by the arrows.

4. DISCUSSION OF RESULTS

Our results on the temperature dependence of the magnetic susceptibility of the first three sulfates show that they all undergo a transition to the antiferromagnetic state at T_C, corresponding to the susceptibility maximum. Hammel[5] carried out a detailed x-ray study (by the powder method) of all the anhydrous sulfates under consideration. He reached the conclusion that their structure is very nearly rhombic with four molecules in the unit cell. The lattice parameters obtained by Hammel are shown in Table III. We do not at

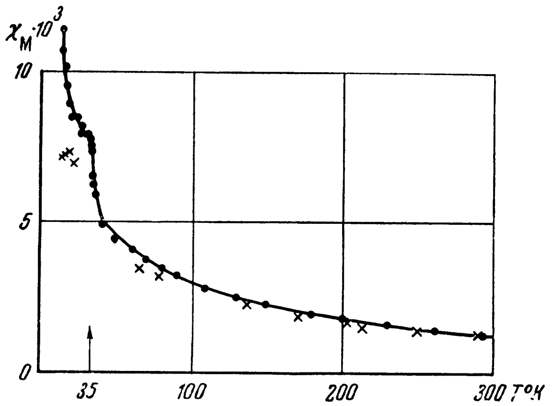

FIG. 2. Temperature dependence of the molar magnetic susceptibility χ_M of anhydrous $CuSO_4$. ×, results of the Leiden laboratory[11]; ●, data from the present work.

present have enough information to determine what the magnetic structure of the sulfates under ininvestigation is in the antiferromagnetic state. This requires x-ray and magnetic studies of monocrystals. However, consideration of the extant data provides a basis for some preliminary conclusions. The lattice of magnetic ions in the anhydrous sulfates can be divided into four sublattices. The arrangement of nearest neighbors about the ions of each of these sublattices will be different. Consequently, the interactions between each pair of sublattices will likewise be different.

In a system of four sublattices it can happen that the interaction between one pair of sublattices differs appreciably from the interaction of another pair. Then, if the two sublattices of the first pair interact in a similar manner to those of the second pair, the ordering of magnetic ions in the first pair of sublattices will occur independently of, and earlier than, the onset of ordering of ions in the other pair. Our observed temperature dependence of the magnetic susceptibility of $CuSO_4$ can be explained by supposing that at $T_C = 35°$ K half the ions undergo a transition to an antiferromagnetic state. Then above this temperature, the magnetic susceptibility will obey the Curie-Weiss law. The quantity Θ will be proportional to the sum of all the interactions. Below the transition point, the susceptibility will be composed of two parts,

$$\chi = \chi_p + \chi_{af} \tag{2}$$

The antiferromagnetic part χ_{af} can be described approximately by the formula

$$\chi_{af} = \frac{C}{6\,(T_C + \Theta)}\left[2 + \left(\frac{T}{T_C}\right)^2\right] \tag{3}$$

The paramagnetic part χ_p can be described as before by the Curie-Weiss law (1), with constants $C' = C/2$ and $\Theta' < \Theta$.

In Fig. 3 our results for $CuSO_4$ are shown as a plot of $1/\chi$ against T. The dotted curve was calculated by formula (2), with the value of Θ' taken as 12°. We see that the outcome of the calculation is not inconsistent with the experimental results. For final confirmation of the proposed interpretation, investigations of the magnetic and thermal properties of $CuSO_4$ at helium temperatures are being undertaken.

Our hypothesis is also supported by experimental results of Stout[12] on the specific heat of $CuSO_4$. Stout observed on the specific heat curve the anomaly characteristic of a second-order phase transition, with a maximum at $T = 34.8°$ K. The experimental value of the entropy corresponding to this anomaly is 0.48 cal degree^{-1} mol^{-1}; this is appreciably less than the theoretical value, $R \ln 2 = 1.377$ cal degree^{-1} mol^{-1}, that should be obtained if all the ions went over to an antiferromagnetic state.

In the last column of Table III are given the values of the effective magnetic moments ($\mu_{eff} = \sqrt{3kC/N\beta^2}$) calculated from our experimental data, and the theoretical values [$\mu_{eff} = 2\sqrt{S(S+1)}$] calculated on the assumption of complete "quenching" of the orbital moment[13]. Comparison of these results shows that for quantitative explanation of the observed values of μ_{eff} in anhydrous slufates, we require a precise calculation of the splitting of the levels by the crystalline field. The crystalline fields have an especially pronounced effect on the magnetic properties of the Co^{++} ion.

In Fig. 4 are shown the results on sulfates of nickel, iron and cobalt, plotted with coordinates $1/\chi$ and T. We see that the experimental points for $NiSO_4$ and $FeSO_4$ deviate negligibly from the straight line corresponding to the Curie-Weiss law. The slight rise in the curve for $NiSO_4$ can be attributed to the effect of short-range order above the Curie point[14]. The results obtained for $FeSO_4$ must be regarded as only qualitative, because of the possible presence in the sample of decomposition products, formed during the calcination. In the case of $CoSO_4$ we observe below 100° K a very

TABLE III

Compound	Lattice parameters[8]				T_C in °K	Ground state of the ion	Effective magnetic moment, μ_{eff}	
	a	b	c	$a:b:c$			Exptl.	Theoret.
$NiSO_4$	4,62	6.51	8.49	0,71 : 1 : 1,30	37	$^3F_4$	3.82	2.83
$CoSO_4$	4.65	6.66	8.46	0.69 : 1 : 1.27	15.5	$^4F_{9/2}$	5.65	3.87
$FeSO_4$	4.82	6.81	8.67	0.71 : 1 : 1.27	21	$^5D_4$	5.20	4.90
$CuSO_4$	4.88	6 66	9,32	0.73 : 1 : 1.25	35	$^2D_{5/2}$	1.91	2.73

appreciable deviation of the experimental curve from the straight line that describes the results in the higher-temperature range. At the transition point, the susceptibility exceeds by almost a factor 2 the value extrapolated along the straight line. The anomalous behavior of the magnetic properties of cobalt is connected with a peculiarity of the splitting of the ground level of the ion by the crystalline field[15,16]. Whereas in the ions Ni^{++}, Fe^{++} and Cu^{++} the splitting of the orbital levels by the crystalline field results in a singlet ground state, in Co^{++} it results in a triplet. This causes a strong anisotropy of the magnetic properties of compounds containing the Co^{++} ion. Each level of the triplet possesses a fourfold spin degeneracy. This degeneracy is removed by spin-orbit interaction, and a Kramers six-doublet system is obtained. Abragam and Pryce[16] showed that the difference between the energies of the lower two doublets may be of the order of 100° K. The calculation of Abragam and Pryce relates to hydrated complex salts of cobalt. However, the pattern of the splitting should be essentially the same in an anhydrous sulfate. The temperature dependence that we have observed in the susceptibility is then easy to explain. At high temperatures, both the lower doublets are filled, and the susceptibility varies in accordance with the Curie-Weiss law. Below 100° K a preferential filling of the lower doublet begins, and this leads to an abrupt deviation from the Curie-Weiss law. At the same time the anisotropy of the magnetic properties should suddenly increase, so that at the Curie point $\chi_{\parallel}$ is several times larger than $\chi_{\perp}$. This causes a sudden decrease of susceptibility below T_C and accounts for the fact that as T approaches 0, the susceptibility approaches a value appreciably smaller than $(2/3) \times \chi(T_C)$.

For anhydrous $NiSO_4$, the Curie point is high enough to permit a conclusion to be drawn from our measurements regarding the law of temperature dependence of the magnetic susceptibility below the Curie point. In Fig. 5 the results of a measurement of the magnetic susceptibility of $NiSO_4$ are shown in coordinates χ and T^2. We see that almost up to the transition temperature itself, the law

$$\chi = a + b(T/T_C)^2, \tag{4}$$

is obeyed, where

$$a \approx 2/3\chi(T_C) \text{ and } b \approx 1/3\chi(T_C).$$

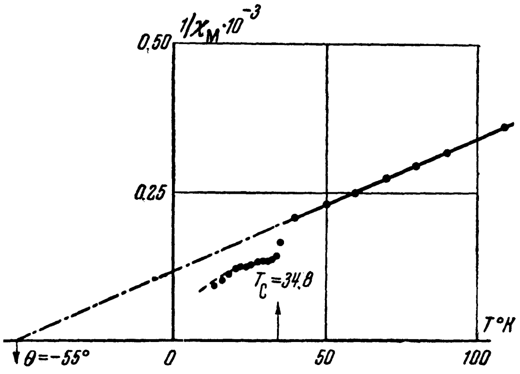

FIG. 3. Temperature dependence of the reciprocal of the molar magnetic susceptibility, $1/\chi_M$, of anhydrous $CuSO_4$. The dotted curve was drawn according to the formula (2).

This result is in agreement with deductions from the theory of spin waves[17,18].

5. CONCLUSIONS

The following basic conclusions can be drawn from this work:

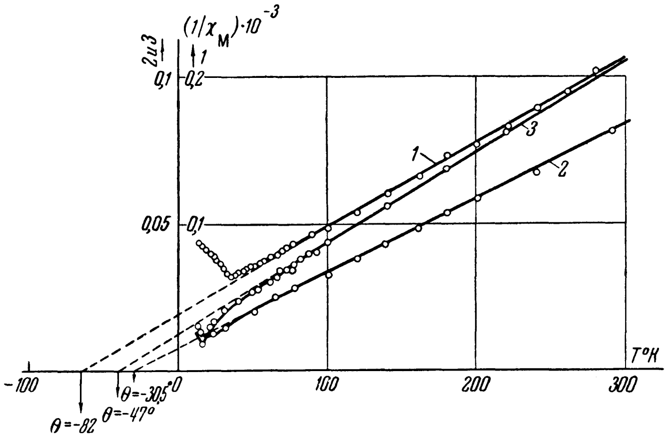

FIG. 4. Temperature dependence of the reciprocal of the molar magnetic susceptibility, $1/\chi_M$ of anhydrous $CuSO_4$. The dotted curve was drawn according to formula (2).

1. It has been shown that the three anhydrous sulfates $NiSo_4$, $FeSO_4$, and $CoSO_4$ undergo a transition to an antiferromagnetic state at temperatures 37, 21, and 15.5 ° K, respectively.

2. The curve of temperature variation of the magnetic susceptibility of $CuSO_4$ displays a sharp break at the temperature 35° K. This anomaly, as well as the general shape of the curve below 35° K, can be explained by supposing that below this temperature half the magnetic copper ions are ordered antiferromagnetically. The other half of the ions remain disordered and cause an increase of susceptibility.

3. The temperature dependence of the magnetic susceptibility of $CoSO_4$ at low temperatures deviates widely from the Curie-Weiss law in the paramagnetic range and displays an anomalously large decrease in the antiferromagnetic range. This is explained qualitatively by the splitting of the ground state of the Co^{++} ion by a crystalline field.

4. It has been shown that over the rather wide temperature interval 14 to 34° K, the magnetic susceptibility of $NiSO_4$ in the antiferromagnetic state varies with temperature according to a quadratic law.

In closing, the authors express their profound thanks to Prof. P. G. Strelkov for his constant interest in the work.

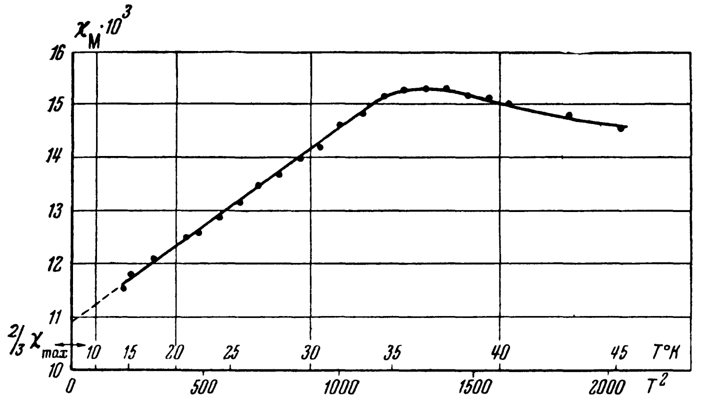

FIG. 5. Temperature dependence of the magnetic susceptibility of the anhydrous sulfate $NiSO_4$ below the Curie point.

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