

## Low-Temperature Magnetic Susceptibilities of the Hydrated Nickel Nitrates\*

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The zero-field magnetic susceptibilities of  $\text{Ni}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  have been measured in the liquid-hydrogen and liquid-helium ranges. The dihydrate is obtained by evaporation of a solution at  $105^\circ\text{C}$ . Its powder susceptibility has a large, sharp, peak at  $4.20^\circ\text{K}$ , where it reaches 0.74 cgs/mole, then drops down to 0.2 cgs/mole below  $2^\circ\text{K}$ . When measured along the  $a$  axis, the susceptibility of monoclinic single crystals of the dihydrate shows a similar peak. It reaches 1.5 cgs/mole, but drops to vanishing values at lower temperatures. The susceptibility in the  $bc$  plane reaches only 0.3 cgs/mole, and is nearly isotropic. It drops little below  $4.20^\circ\text{K}$ . This behavior is similar to that of  $\text{FeCl}_2$ , or  $\text{FeCO}_3$ , and suggests the existence of two magnetic sublattices, with strong ferromagnetic interactions within each sublattice, and weaker antiferromagnetic interactions between one sublattice and the other (metamagnetism). A spin Hamiltonian with  $S=1$  and uniaxial one-ion anisotropy gives results in fair agreement with the experimental data if the exchange interactions are described in the molecular-field approximation. The best fit corresponds to  $g=2.25$ ,  $D/k=-6.50^\circ\text{K}$ ,  $n_1=+0.32$  mole/cgs,  $n_2=-2.12$  mole/cgs, where  $n_1$  and  $n_2$  are, respectively, the antiferromagnetic and the ferromagnetic molecular-field constants. In the case of the tetrahydrate and of the hexahydrate, the powder susceptibility approaches a constant value of 0.35 cgs/mole below  $2^\circ\text{K}$ ; the data can be fitted to the spin Hamiltonian for a nickel ion in a rhombic field, without exchange, with  $E/k=-2.66^\circ\text{K}$ ,  $D/k=-8.67^\circ\text{K}$ , and  $g=2.25$ .

### INTRODUCTION

IN spite of, and partly because of, their low symmetry, many hydrated salts of elements of the first transition series, hitherto ignored, should be interesting objects for magnetic investigations at low temperature. Exchange interactions among paramagnetic ions in these materials are weak but often large enough to produce cooperative spin ordering above  $1^\circ\text{K}$  as has already been shown in several instances beginning with the well-known example of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  ( $T_N=4.3^\circ\text{K}$ ). The possibility thus arises in compounds containing, for example,  $\text{Ni}^{++}$ , that the exchange interactions may be of the same order of magnitude as the zero-field splitting of the single-ion ground state, i.e., comparable with the single-ion anisotropy energy. We wish to report the investigation of the magnetic susceptibilities at low temperature of the hydrates of nickel nitrate. One of them,  $\text{Ni}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , exhibits cooperative long-range spin order below  $4.20^\circ\text{K}$ , and provides an interesting example of the case just mentioned. A detailed model of the behavior of this substance is proposed.

### DESCRIPTION OF THE SAMPLES

According to Sieverts and Schreiner,<sup>1</sup> the salt obtained by evaporation of an aqueous solution of nickel nitrate between  $-27.8$  and  $-3^\circ\text{C}$  is the enneahydrate (nine waters). Between  $-3$  and  $54.0^\circ\text{C}$  it is the hexahydrate. Between  $54.0$  and  $85.4^\circ\text{C}$ , the tetrahydrate is obtained. The dihydrate crystallizes out above  $85.4^\circ\text{C}$ . Before the work of Sieverts and Schreiner, the tetrahydrate was thought to be a trihydrate, and the existence of the dihydrate was doubtful.

The material used in the present investigations was

\* Work supported in part by the U. S. Office of Naval Research, and the National Science Foundation.

<sup>1</sup>A. Sieverts and L. Schreiner, *Z. Anorg. Allgem. Chem.* **219**, 105 (1934).

obtained from the J. T. Baker Chemical Company, in the "Baker Analyzed Reagent" grade, and the Fisher Scientific Company, in the "Fisher Certified" grade.

All samples were recrystallized from solution in order to insure the proper degree of hydration. We did not study the enneahydrate. The hexahydrate was recrystallized by evaporation of a water solution at room temperature. The tetrahydrate was recrystallized by evaporation around  $70^\circ\text{C}$ . The dihydrate was recrystallized by evaporation of the solution near  $105^\circ\text{C}$ . We noticed in the latter case a strong tendency of the solution to decompose at the surface where it is in contact with the air.

The crystals of the hexahydrate are monoclinic. Only the macroscopic morphology is known.<sup>2</sup> The crystal structure of the tetrahydrate is entirely unknown; we found the crystals to have the shape of flat rhombs.

An investigation of the structure of the dihydrate by x-ray methods is in progress.<sup>3</sup> The crystals belong to the  $P2_1/C$  monoclinic space group.<sup>4</sup> The unit cell has the following characteristics:  $a=5.79\text{\AA}\pm 0.02$ ;  $b=5.90\text{\AA}\pm 0.02$ ;  $c=8.51\text{\AA}\pm 0.04$ ;  $\beta=91.1^\circ\pm 0.2$ . The density as measured directly<sup>3</sup> is  $2.46\text{ g/cm}^3$ . This agrees with the x-ray density 2.50 obtained by assuming two molecules per unit cell. The crystals have the shape of needles with rhombic cross section. The  $a$  axis is parallel to the

<sup>2</sup>C. F. Rammelsberg, *Handbuch der Krystallographisch-physikalischen Chemie* (Engelmann, Leipzig, 1881), Vol. 1, p. 360. It should however be noted that several phase transitions have been observed below room temperature in the hexahydrate. See J. Jaffray and N. Rodier, *Compt. Rend.* **238**, 1975 (1954); *J. Rech. Centre Natil. Rech. Sci.* **31**, p. 252 (1955). Some of them may be associated with the rotation of water molecules or of nitrate groups in the crystal.

<sup>3</sup>We want to express our thanks to R. Baughman and to Dr. G. A. Jeffrey of the University of Pittsburgh for the communication of their results.

<sup>4</sup>N. F. M. Henry and K. Lonsdale, *International Tables for X-Ray Crystallography* (The Kynoch Press, Birmingham, England, 1952), Vol. 1, p. 99.

needle axis. The monoclinic  $b$  axis is parallel to the short diagonal of the rhomb, and the  $c$  axis is almost parallel to the large diagonal. As the monoclinic angle  $\beta$  is very close to  $90^\circ$ , the crystal may appear superficially to be orthorhombic. The  $bc$  plane, which is almost normal to the needle axis, is a good cleavage plane. The crystals have a tendency to cleave spontaneously along this plane, and this provides paths through which atmospheric water can penetrate the crystals, so that they deteriorate, usually after a few days.

X-ray analysis has shown<sup>8</sup> that the crystals of the dihydrate have a very strong tendency to twin on an almost microscopic scale. Even the small crystals suitable for x-ray work are usually twinned at least once. The larger crystals (0.010–0.015 g) used in our susceptibility measurements are probably always twinned a large number of times. The two parts of a twin seem to be related to each other by a  $180^\circ$  rotation around an axis perpendicular to the  $bc$  plane. The twinning is probably due in part to the weakness of the bonding between successive  $bc$  layers. We will see later that it is not likely to have much influence on the magnetic properties of the crystal.

Preliminary values of the coordinates<sup>8</sup> of atoms in the unit cell of the dihydrate are given in Table I. When the coordinates of the first six atoms of the table are known, the coordinates of all others can be found by using the operations of the symmetry group of the crystal. The nickel atoms are located at the corners of the unit cell, and also at the center of the  $a$  faces of the cell, as shown in Figs. 1 and 2. Each nickel atom is surrounded by four oxygen atoms belonging to four different  $\text{NO}_3^-$  groups, and by two water molecules. As shown on Fig. 1, a

TABLE I. Preliminary values of the coordinates of atoms in the unit cell of nickel nitrate dihydrate. The numbers are expressed as fractions of the length of the axes  $a$ ,  $b$ ,  $c$  of the monoclinic cell. The origin is located at a corner of the cell.

Atom	Along $a$	Along $b$	Along $c$
Oxygen	0.0476	0.136	0.227
Nitrogen	0.241	0.168	0.293
Oxygen (water)	0.757	0.247	0.486
Nickel	0.000	0.000	0.000
Oxygen	0.257	0.284	0.422
Oxygen	0.424	0.087	0.241
Nickel	0.000	0.500	0.500
Oxygen (water)	0.243	0.747	0.014
Oxygen (water)	0.757	0.253	0.986
Oxygen (water)	0.243	0.753	0.514
Nitrogen	0.241	0.332	0.793
Nitrogen	0.759	0.668	0.207
Nitrogen	0.759	0.832	0.707
Oxygen	0.0476	0.364	0.727
Oxygen	0.257	0.216	0.922
Oxygen	0.424	0.413	0.741
Oxygen	0.9524	0.864	0.773
Oxygen	0.743	0.716	0.578
Oxygen	0.576	0.913	0.759
Oxygen	0.9524	0.636	0.273
Oxygen	0.743	0.784	0.078
Oxygen	0.576	0.587	0.259

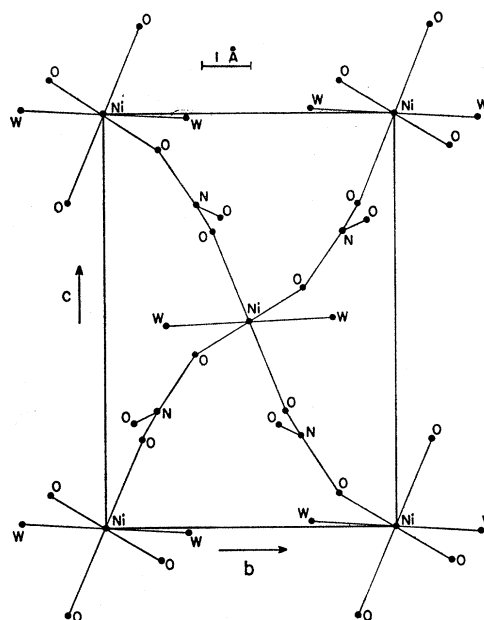


FIG. 1. Projection of the unit cell of nickel nitrate dihydrate on the  $bc$  plane. The nickel ions form a face-centered pattern. The symbol W is used to describe a water molecule.

nickel atom is directly connected by a  $\text{NO}_3^-$  group to each of the four nearest nickel atoms, located in the same  $bc$  plane. On the other hand, linkage from one nickel atom to another nickel atom located in a different  $bc$  layer is more indirect, and has to go at least through two  $\text{NO}_3^-$  groups (Fig. 2). This will be of importance for the interpretation of the magnetic properties of the crystal. The easy cleavage along the  $bc$  plane indicates also that bonds between successive  $bc$  sheets are relatively weak.

In order to check the correctness of the degree of hydration, crystals of the three salts have been submitted to a quantitative chemical analysis, performed by Galbraith Laboratories, Inc. The results are given in Table II. Only the hydrogen, nitrogen, and nickel mass percentages have been determined. The oxygen percentage has been derived by subtraction from 100%.

TABLE II. Results of quantitative chemical analysis, expressed in mass percentages, and compared with the theoretical value derived from the chemical formula. The oxygen percentage has not been determined by analysis, but has been derived from the other percentages by subtraction from 100%.

		%H	%N	%Ni	%O
Hexahydrate	Analysis	6.12	8.88	20.29	64.71
	Formula	4.16	9.63	20.19	66.02
Tetrahydrate	Analysis	5.53	11.39	23.03	60.05
	Formula	3.16	11.00	23.04	62.8
Dihydrate	1st Analysis	5.55	11.57	24.94	57.94
	2nd Analysis	4.98	11.98	26.74	56.30
	Formula	1.84	12.81	26.84	58.51

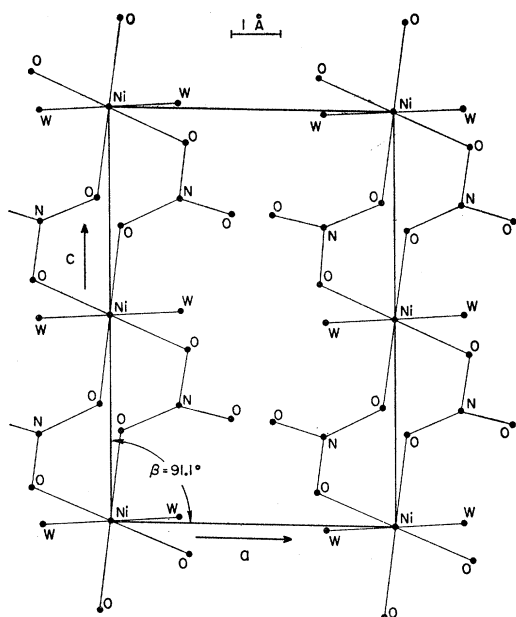


FIG. 2. Projection of the unit cell of nickel nitrate dihydrate on the  $ac$  plane.

The measured nickel percentages agree quite well with those calculated from the formula in most cases. As quantitative chemical analysis is known to be easiest and most reliable in the case of metal ions, this agreement is evidence that the chemical composition of our crystals (including the degree of hydration) is indeed as stated.

#### EXPERIMENTAL PROCEDURE

Magnetic susceptibilities have been measured by means of a mutual inductance bridge, working usually at 275 cps. This bridge is similar to that described by Pillinger, Jastram, and Daunt.<sup>5</sup> The small change of mutual inductance produced by insertion of the sample into the coil is proportional to the susceptibility of the sample. The bridge is calibrated during each run against a sample of powdered manganous ammonium sulphate, the susceptibility of which is given<sup>6</sup> by  $\chi = 0.01119/T$  cgs/g.

In the case of powder measurements, the sample is packed in a thin-walled soft-glass sphere supported by a thin nylon or silk thread. The mass of the sample lies between 0.2 and 0.4 g. In the case of single-crystal measurements, the sample is tied with silk thread to a 20-mm-long Lucite rod of square cross section, suspended by a silk thread. The mass of the crystal is only 0.010–0.015 g.

In the 14–20°K range and in the 1.3–4.2°K range, the

<sup>5</sup> W. L. Pillinger, P. S. Jastram, and J. G. Daunt, *Rev. Sci. Instr.* **29**, 159 (1958).

<sup>6</sup> A. H. Cooke, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. 1, p. 238.

sample and the mutual inductance coil are in direct contact with a liquid-hydrogen bath, or with a liquid-helium bath.

In the range between 4.2 and 14°K, we have used an apparatus which allows the sample to be heated above the temperature of the bath (Fig. 3). A soft-glass vacuum jacket is connected to a mechanical pump, which gives only an imperfect vacuum. The heat losses through this vacuum jacket are compensated by the constant heat produced by an electric heater, made of manganin wire, which extends all along the walls of the experimental space. The sample is supported by a  $\frac{1}{16}$ -in. nylon rod which may be moved up and down from the top of the cryostat. The experimental space is filled with a few mm Hg or cm Hg of helium exchange gas, to promote uniformity of temperature. The sample of powdered manganese ammonium sulphate, which is used to calibrate the bridge, is also used as a magnetic thermometer to measure the temperature in the experimental space. The valves controlling the pressure in the vacuum jacket and in the experimental space are kept closed during the measurements themselves, in order to minimize the fluctuations of pressure and temperature. This apparatus has been partly designed and built by Pierce.

#### DISCUSSION OF THE RESULTS ON THE HEXA-HYDRATE AND ON THE TETRAHYDRATE

The experimental results for nickel nitrate hexahydrate are shown in Fig. 4. The susceptibility has been

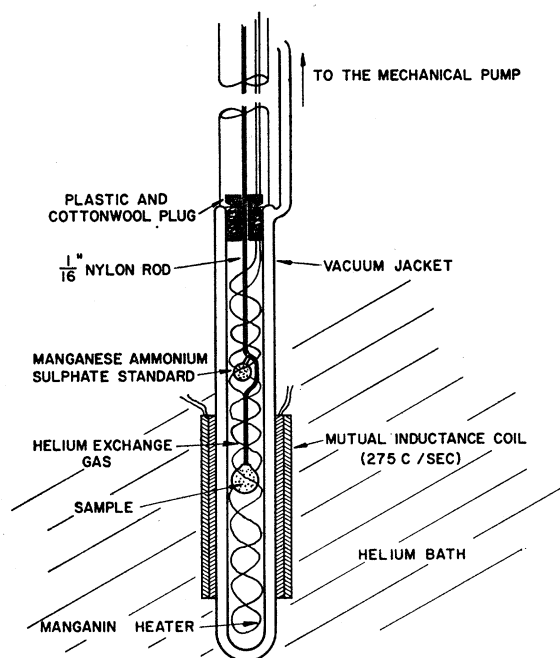


FIG. 3. Apparatus with a vacuum jacket, used in the range between 4.2 and 14°K. A manganin heater extends all along the walls of the experimental space, and permits the temperature to be kept at any desired level. The manganese ammonium sulphate standard is used as a magnetic thermometer.

measured on the powder only. Similar behavior has been observed in other dilute nickelous salts. It can be described<sup>7</sup> by a spin Hamiltonian for  $S=1$  without exchange, assuming rhombic symmetry:

$$H = +DS_z^2 + E(S_x^2 - S_y^2) + g\beta\mathbf{S} \cdot \mathbf{H}. \quad (1)$$

The powder susceptibility  $\chi_p$  derived from Eq. (1) is

$$\chi_p = \frac{2Ng^2\beta^2}{3(D^2 - E^2)} \frac{2D - \exp(-D/kT)[(3E^2 - D^2/E)\sinh(E/kT) + 2D \cosh(E/kT)]}{1 + 2 \exp(-D/kT)\cosh(E/kT)}. \quad (2)$$

We have fitted Eq. (2) to our experimental results for the hexahydrate, using a program written by J. T. Schriempf for the Bendix G-20 computer at the Carnegie Institute of Technology. The results of the fit (see Fig. 4) is:  $E/k = -2.66^\circ\text{K}$ ;  $D/k = -8.67^\circ\text{K}$ ;  $g = 2.25$ . This value of  $D/k$  is higher than the values reported<sup>8-10</sup> for other nickelous salts by at least 50%. This may be due to a low symmetry environment of the nickel ion in nickel nitrate hexahydrate. Most of the other nickelous salts which have been investigated have an octahedral environment of water molecules of almost cubic symmetry around the nickel ion. Our value for the  $g$  factor is similar to the value found for other nickelous salts.

The experimental results for the tetrahydrate are shown on Fig. 5. Again, the measurements have been made only on the powder. They include, however, the interval between 4 and  $14^\circ\text{K}$ ; the special apparatus with vacuum jacket, described previously, was used in that range.

The values of the molar susceptibility of the tetrahydrate and of the hexahydrate are practically identical. The theoretical curve of Fig. 4 has also been drawn on

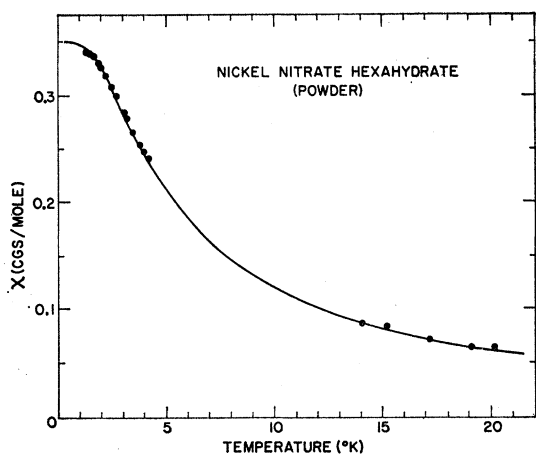


Fig. 4. Powder susceptibility of nickel nitrate hexahydrate as a function of temperature. The solid curve is the theoretical prediction for an  $S=1$  paramagnet with  $E/k = -2.66^\circ\text{K}$ ;  $D/k = -8.67^\circ\text{K}$ ;  $g = 2.25$ .

<sup>7</sup> T. Haseda and M. Date, J. Phys. Soc. Japan **13**, 175 (1958).

<sup>8</sup> J. H. E. Griffiths, and J. Owen, Proc. Roy. Soc. (London) **A213**, 459 (1952).

<sup>9</sup> M. Date, Sci. Rep. Res. Inst. Tohoku Univ. **A6**, 390 (1954).

<sup>10</sup> T. Watanabe, J. Phys. Soc. Japan **17**, 1856 (1962).

Fig. 5, with the same values of the parameters, and is seen to fit the data fairly well. This might suggest that the environment of the nickel ion is the same in the tetrahydrate and in the hexahydrate. Only an x-ray determination of the structure of these salts can give a definitive proof of this, of course. We should notice also that the existence of sizeable exchange interactions in the hexahydrate and in the tetrahydrate cannot be excluded on the sole basis of our powder susceptibility measurements. Single crystal measurements similar to those performed by Watanabe<sup>10</sup> on the nickel sulphates would shed light on this point. These, however, should probably await the determination of the structures of the salts.

The powder susceptibility of the hexahydrate has also been measured by Janes<sup>11</sup> down to  $80^\circ\text{K}$ . His results correspond to  $g = 2.26$  and a Curie-Weiss constant  $\Theta$  somewhere between  $-4$  and  $0^\circ\text{K}$ . This agrees well with the present measurements. The measurements by Johnson and Grayson-Smith<sup>12</sup> extend also down to  $80^\circ\text{K}$ , and correspond to  $g = 2.02$  and  $\Theta = +21^\circ\text{K}$ . These values, especially the low splitting factor, appear anomalous.

#### DISCUSSION OF THE RESULTS ON THE DIHYDRATE

The experimental results for the dihydrate are shown in Fig. 6. The powder susceptibility  $\chi_p$  has a large sharp peak at  $4.20^\circ\text{K}$ , very close to the boiling point of helium under atmospheric pressure. Only one side of the peak was investigated with the sample in contact with the helium bath. The other side of the peak was examined by means of the apparatus with vacuum jacket, described above. The results obtained with the two experimental arrangements have been found to agree at  $4.20^\circ\text{K}$  and in the  $14$ – $20^\circ\text{K}$  liquid-hydrogen range, where both can be used.

Because of the smallness of the samples, single-crystal measurements have been performed only with the simple apparatus, which happens to be the most sensitive one. The susceptibility  $\chi_a$  along the  $a$  axis (needle axis) seems to have a very sharp and very large peak at  $4.20^\circ\text{K}$ . It drops, however, below the powder susceptibility at temperatures lower than  $2.7^\circ\text{K}$ , and seems almost to vanish at the absolute zero. On the

<sup>11</sup> R. B. Janes, Phys. Rev. **48**, 78 (1935).

<sup>12</sup> A. F. Johnson and H. Grayson-Smith, Can. J. Res. **28A**, 234 (1950).

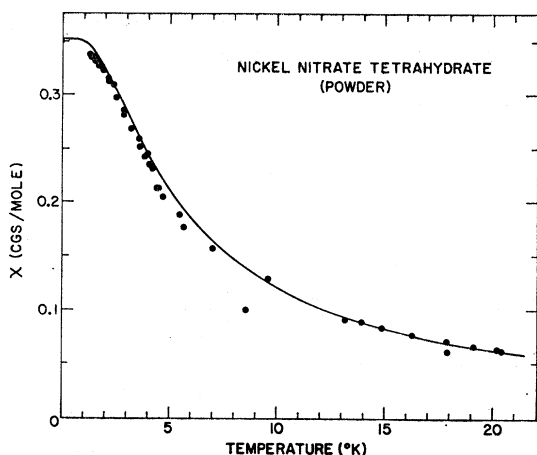


FIG. 5. Powder susceptibility of nickel nitrate tetrahydrate as a function of temperature. The solid curve is the theoretical prediction for an  $S=1$  paramagnet with  $E/k=-2.66^\circ\text{K}$ ;  $D/k=-8.67^\circ\text{K}$ ;  $g=2.25$ .

contrary,  $\chi_b$  and  $\chi_c$  vary very little below  $4.20^\circ\text{K}$ . Their relative difference is only 5% in the helium range. This suggests that the susceptibility tensor has approximate rotational symmetry around the  $a$  axis. This suggestion is confirmed by a measurement (not shown in Fig. 6) done at  $4.2^\circ\text{K}$  in a direction in the  $bc$  plane which is at  $45^\circ$  to the  $b$  axis. It is also confirmed by some rough measurements done at  $4.2^\circ\text{K}$  in various directions at  $45^\circ$  to the  $a$  axis. As an additional check, a special device was built which allows one to rotate the crystal during the measurements. By rotating around the monoclinic  $b$  axis at  $4.2^\circ\text{K}$ , the susceptibility in the  $ac$  plane is found to pass through a maximum along the  $a$  axis, with an error of less than  $5^\circ$ . Therefore, as the monoclinic angle  $\beta$  is very close to  $90^\circ$ ,  $\chi_a$ ,  $\chi_b$ , and  $\chi_c$

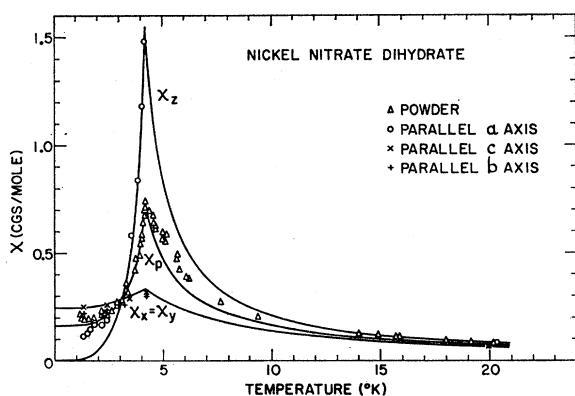


FIG. 6. Powder susceptibility  $\chi_p$  and single-crystal susceptibilities  $\chi_a$ ,  $\chi_b$ ,  $\chi_c$  of nickel nitrate dihydrate as a function of temperature. The solid curves  $\chi_p$ ,  $\chi_x=\chi_y$ ,  $\chi_z$ , are theoretical predictions for an  $S=1$  metamagnet with  $E/k=0$ ;  $D/k=-6.50^\circ\text{K}$ ;  $n_1=+0.321$  mole/cgs;  $n_2=-2.122$  mole/cgs;  $g=2.250$ ; where  $n_1$  and  $n_2$  are the molecular field constants for the antiferromagnetic and the ferromagnetic interaction.  $Oz$  is parallel to the  $a$  axis of the crystal;  $Ox$  to the  $b$  axis, and  $Oy$  is approximately parallel to the  $c$  axis.

are practically equal to the principal values of the susceptibility tensor. As a word of caution, it should be said that most of these tests have been performed only at  $4.2^\circ\text{K}$ , and therefore do not really exclude changes of the directions of the principal axes with temperature.

A first clue to the interpretation of our susceptibility measurements is given by a plot of the inverse powder susceptibility against temperature (Fig. 7). Between 5 and  $20^\circ\text{K}$ , the experimental points fall on a straight line corresponding to  $\chi_p=1.41/(T-2.5)$  cgs/mole. For a spin  $S=1$ , this leads to  $g=2.38$ . The positive value  $2.5^\circ\text{K}$  of the Curie-Weiss temperature indicates the predominance of ferromagnetic exchange interactions. The reasonable value of the  $g$  factor excludes the possibility of canted antiferromagnetism. Simple ferromagnetism would probably lead to higher values of the susceptibility than actually observed below the Curie point, due to domain wall motion. A possibility which remains is the simultaneous existence of strong ferromagnetic and weaker antiferromagnetic interactions in the same crystal.

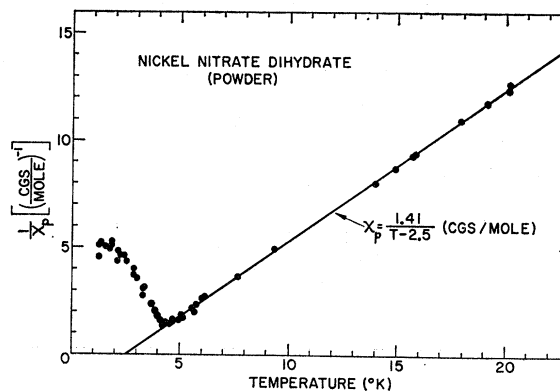


FIG. 7. Reciprocal of the powder susceptibility  $\chi_p$  of nickel nitrate dihydrate, as a function of temperature.

Our experimental curves (Fig. 6) are very similar to those found<sup>13,14</sup> for  $\text{FeCl}_2$  and  $\text{FeCO}_3$ . These compounds have layer structures. Below the Curie point, magnetic ions of one layer are kept in parallelism by a rather strong ferromagnetic exchange interaction. A weaker antiferromagnetic interaction exists between successive layers, so that no net magnetic moment develops in zero applied field. Due to the anisotropy of exchange, or to ion anisotropy, or to magnetic dipole interactions, there is a preferred axis for the spins, normal to the ferromagnetic layers. In some different layer structures, there is rather a preferred plane, parallel to the layers.

Two-sublattice theories have been developed by

<sup>13</sup> H. Bizette, C. Terrier, and B. Tsai, *Compt. Rend.* **243**, 895 (1956); C. Starr, F. Bitter and A. R. Kaufmann, *Phys. Rev.* **58**, 977 (1940); M. K. Wilkinson, J. W. Cable, E. O. Wollan, and W. C. Koehler, *ibid.* **113**, 497 (1959).

<sup>14</sup> I. S. Jacobs, *J. Appl. Phys.* **34**, 1106 (1963).

several authors for these layer compounds,<sup>15-20</sup> using the molecular-field approximation, or the Ising approximation, or even the Bethe-Peierls approximation.

These compounds are often called<sup>16,17</sup> metamagnets, due to the abrupt transition to simple ferromagnetism exhibited in a moderate external field.

The idea that nickel nitrate dihydrate is a layer compound agrees not only with its magnetic properties, but also with direct structural evidence. As we have seen in a previous section of the present paper, a nickel ion is directly connected by a nitrate group to each of the four nearest nickel ions, which are located in the same *bc* sheet. On the other hand, interaction between nickel ions belonging to two successive *bc* sheets is more indirect, and probably weaker.

#### SUSCEPTIBILITY OF A $S=1$ METAMAGNET IN THE MOLECULAR-FIELD APPROXIMATION

We will derive an expression for the zero-field susceptibility of a  $S=1$  metamagnet in the molecular-field approximation, assuming only a single-ion anisotropy, and no anisotropic exchange. We will show that the results are in fair agreement with our susceptibility measurements in nickel nitrate dihydrate, for reasonable values of the parameters. The ratio of the anisotropic part of the exchange energy to the isotropic part is in general of the order of  $(g-2/2)^2$  and is therefore rather small. The study of the hexahydrate and of the tetrahydrate made in the preceding sections suggests on the contrary that the single-ion anisotropy energy, as represented by the parameter  $D$ , may be of the order of several degrees Kelvin in the nickel nitrates, and therefore would be comparable to the isotropic exchange energy. Kanamori and other authors<sup>18-20</sup> have even assumed that the single-ion anisotropy energy is much larger than the isotropic exchange energy in  $\text{FeCl}_2$ ; this is not likely to be true in nickel nitrate dihydrate, and the methods used by these authors cannot be applied to this case.

As the susceptibility of nickel nitrate dihydrate has almost uniaxial symmetry around the  $\alpha$  axis, we can assume a zero value for the parameter  $E$  which describes the rhombic part of the one-ion anisotropy. The spin Hamiltonian of a nickel ion<sup>21</sup> is

$$H = DS_z^2 + g\beta\mathbf{S} \cdot \mathbf{H}, \quad (3)$$

where  $\mathbf{H}$  is the effective field, which includes the molecular field. The orthogonal system of coordinates

$Oxyz$  is such that  $Oz$  is parallel to the  $a$  axis of the crystal (needle axis) and  $Ox$  to the  $b$  axis.  $Oy$  is then almost parallel to the  $c$  axis. We assume  $D < 0$ , which implies that  $Oz$  is a preferred direction for the spins.

Our introduction of the parameter  $D$  neglects the fact that there are two nonequivalent nickel ions per unit cell. It gives only a description of the anisotropy as averaged over the two ions. It is also assumed to include in an approximate manner the effects of dipolar magnetic interaction.

According to the preliminary structural data (Table I), the distances from a nickel ion to the four nearest oxygen ions belonging to nitrate groups are equal to 2.11 or 2.06 Å, while the distance to the two nearest oxygens belonging to water molecules is equal to 2.06 Å. The differences between these values amount to only 2.5%, and are probably within the range of experimental uncertainty. The water molecules are neutral, but have strong electric dipole moments. At the same time, each nitrate group carries one negative electron charge. This suggests that the water molecules and the oxygens belonging to nitrate groups produce quite different electric fields. Then the local crystal field at the nickel ion would have rotational symmetry around the axis passing through the water molecules. This crystal field axis makes an angle of approximately  $50^\circ$  with the  $a$  axis. The crystal field axes at the two nonequivalent nickel ions are almost exactly related by a  $180^\circ$  rotation around the  $a$  axis. After averaging over the two ions, the anisotropy properties of the crystal are therefore expected to have an approximate twofold symmetry around the  $a$  axis. This is at least compatible with the higher degree of symmetry around the  $Oz = a$  axis exhibited by our Hamiltonian of Eq. (3). It implies also that the twinning, which amounts to a  $180^\circ$  rotation of one part of the crystal around an axis normal to the *bc* plane, will practically not change the magnetic properties of the crystal. The preceding interpretation of the crystal field is, of course, only tentative.

There are two magnetic sublattices,  $A$  and  $B$ , which may probably be identified with successive layers parallel to the easy cleavage plane *bc*. In the molecular-field approximation,<sup>17</sup> the effective field  $\mathbf{H} = \mathbf{H}_A$  acting on a spin of  $A$  is different from the effective field  $\mathbf{H} = \mathbf{H}_B$  acting on a spin of  $B$ :

$$\begin{aligned} \mathbf{H}_A &= \mathbf{H}_0 - n_1 \mathbf{M}_B(\mathbf{H}_B, T) - n_2 \mathbf{M}_A(\mathbf{H}_A, T), \\ \mathbf{H}_B &= \mathbf{H}_0 - n_1 \mathbf{M}_A(\mathbf{H}_A, T) - n_2 \mathbf{M}_B(\mathbf{H}_B, T), \end{aligned} \quad (4)$$

where  $\mathbf{H}_0$  is the applied magnetic field, and  $\mathbf{M}_A$ ,  $\mathbf{M}_B$  the magnetization of sublattice  $A$  and  $B$  expressed in cgs units per mole of magnetic ions. The observed bulk magnetization is  $\mathbf{M} = \frac{1}{2}(\mathbf{M}_A + \mathbf{M}_B)$ . Introducing the sublattice magnetization  $\mathbf{M}_0$  in zero applied field, we can write

$$\mathbf{M}_A = \mathbf{M}_0 + \mathbf{M}; \quad \mathbf{M}_B = -\mathbf{M}_0 + \mathbf{M}.$$

The energy levels of an ion in a finite effective field

<sup>15</sup> L. Landau, *Physik. Z. Sowjetunion* 4, 675 (1933).

<sup>16</sup> L. Néel, *Nuovo Cimento Suppl.* 6, 942 (1957).

<sup>17</sup> A. Herpin, in *Low Temperature Physics*, edited by C. DeWitt, B. Dreyfus, and P. G. de Gennes (Gordon and Breach Publisher, Inc., New York, 1962) p. 309.

<sup>18</sup> J. Kanamori, *Progr. Theoret. Phys. (Kyoto)* 20, 890 (1958).

<sup>19</sup> S. Yomosa, *J. Phys. Soc. Japan* 15, 1068 (1960).

<sup>20</sup> B. R. Heap, *Proc. Phys. Soc. (London)* 80, 248 (1962).

<sup>21</sup> Our parameter  $D$  is the same as that of Haseda and Date (see Ref. 7). Watanabe puts a minus sign in front of  $D$  and  $E$  in his Hamiltonian (see Ref. 10).

$\mathbf{H}=\mathbf{H}_A$  or  $\mathbf{H}=\mathbf{H}_B$  parallel to  $Oz$  may be derived<sup>7</sup> from Eq. (3):

$$W_1=+D+g\beta H_z; \quad W_2=+D-g\beta H_z; \quad W_3=0.$$

From them, the expression for  $\mathbf{M}_A$  and the similar expression for  $\mathbf{M}_B$  may be computed, using elementary statistical mechanics; for example,

$$(M_A)_z = Ng\beta \frac{2 \sinh(g\beta H_A/kT)}{\exp(+D/kT) + 2 \cosh(g\beta H_A/kT)},$$

$$(M_A)_x = (M_A)_y = 0.$$

These expressions for  $\mathbf{M}_A(\mathbf{H}_A, T)$  and  $\mathbf{M}_B(\mathbf{H}_B, T)$  may be substituted into Eqs. (4).

Assuming a zero applied magnetic field, the self-consistent Eqs. (4) give for the sublattice magnetization

$$\chi_z = \frac{(M)_z}{(H_0)_z} = \left[ \left( \frac{kT}{2Ng^2\beta^2} \right) \frac{[\exp(D/kT) + 2 \cosh(g\beta(n_1-n_2)M_0/kT)]^2}{2 + \exp(D/kT)\cosh(g\beta(n_1-n_2)M_0/kT)} + (n_1+n_2) \right]^{-1}. \quad (7)$$

The self-consistent Eqs. (4) may be solved in the presence of a small applied magnetic field  $\mathbf{H}_0$  parallel to  $Ox$ . As the effective field  $\mathbf{H}$  acting on a ion is not parallel to  $Oz$  any more, it will mix together the three zero-field states of the system, and it is necessary to use perturbation theory to find the energy levels and the expression of the functions  $\mathbf{M}_A(\mathbf{H}_A, T)$  and  $\mathbf{M}_B(\mathbf{H}_B, T)$ . The  $z$  component of  $\mathbf{H}$  is constant, and is entirely due to the molecular field set up by the sublattice magnetization. The energy levels are

$$\begin{aligned} W_1 &= D + g\beta H_z - g^2\beta^2 H_x^2 \left( \frac{1}{2} / (-D - g\beta H_z) \right), \\ W_2 &= D - g\beta H_z - g^2\beta^2 H_x^2 \left( \frac{1}{2} / (-D + g\beta H_z) \right), \\ W_3 &= g^2\beta^2 H_x^2 \left( \frac{1}{2} / (-D - g\beta H_z) \right) \\ &\quad + g^2\beta^2 H_x^2 \left( \frac{1}{2} / (-D + g\beta H_z) \right). \end{aligned}$$

This gives for  $\mathbf{M}_A$ , for example,

$$\begin{aligned} (M_A)_z &= M_0, \quad (M_A)_y = 0, \\ (M_A)_x &= Ng^2\beta^2 (H_A)_x \frac{((e^a-1)/akT) + ((e^b-1)/bkT)}{1 + e^a + e^b}, \end{aligned}$$

where

$$a = (-D + g\beta(n_1 - n_2)M_0)/kT$$

and

$$b = (-D - g\beta(n_1 - n_2)M_0)/kT.$$

Substituting this expression of  $\mathbf{M}_A(\mathbf{H}_A, T)$ , and a similar expression for  $\mathbf{M}_B(\mathbf{H}_B, T)$ , into Eqs. (4), we get for the reciprocal of the observed zero-field susceptibility

$$\chi_x^{-1} = \chi_y^{-1} = \frac{(H_0)_x}{(M)_x} = \frac{1 + e^a + e^b}{Ng^2\beta^2 [(e^a-1)/akT + (e^b-1)/bkT] + (n_1+n_2)}. \quad (8)$$

$\mathbf{M}_0$ , which is parallel to  $Oz$ :

$$M_0 = Ng\beta \frac{2 \sinh[g\beta(n_1-n_2)M_0/kT]}{\exp(D/kT) + 2 \cosh[g\beta(n_1-n_2)M_0/kT]}. \quad (5)$$

Writing the condition for Eq. (5) to have a small, nonvanishing solution  $M_0$ , we can find also the equation determining the Curie point  $T_c$  of the metamagnet:

$$2 + \exp(-d/t_c) - 1/t_c = 0, \quad (6)$$

where

$$\begin{aligned} d &= -D/2Ng^2\beta^2(n_1-n_2), \\ t_c &= kT_c/2Ng^2\beta^2(n_1-n_2). \end{aligned}$$

The self-consistent Eqs. (4) may be solved in the presence of a small applied magnetic field  $\mathbf{H}_0$  parallel to  $Oz$ , giving an expression for the observed parallel zero-field susceptibility  $\chi_z$ :

Using a numerical method and the G-20 Bendix computer at Carnegie Institute of Technology, we have solved Eq. (6), which determines the Curie point  $T_c$ . The results are given in Table III, for various values of the dimensionless anisotropy parameter

$$d = -D/2Ng^2\beta^2(n_1-n_2).$$

Then, using the G-20 computer, we have fitted Eqs. (7) and (8) to our experimental data on the single-crystal susceptibility and the powder susceptibility  $\chi_p = \frac{1}{3}\chi_z + \frac{2}{3}\chi_x$  of nickel nitrate dihydrate, at the Curie point and above (see Fig. 6). The fit is easier in this temperature range, as the sublattice magnetization  $M_0$  vanishes. The result of the fit is:  $D/k = -6.50^\circ\text{K}$ ;  $n_1 = +0.321$  mole/cgs;  $n_2 = -2.122$  mole/cgs,  $g = 2.250$ . It is to be noticed that these values have been chosen in such a way as to satisfy the additional requirement of leading to the correct value of  $T_c$  when substituted into Eq. (6) (see Table III); this value is assumed to be:  $T_c = 4.20^\circ\text{K}$ .

The value found for the  $g$  factor is equal to that found for the tetrahydrate and the hexahydrate. The value for  $D/k$  is also of the same order of magnitude as in these salts. The ratio  $|n_2/n_1|$  of the intralayer ferro-

TABLE III. Reduced temperature  $t_c = kT_c/2Ng^2\beta^2(n_1-n_2)$  of the Curie point of a  $S=1$  metamagnet, as obtained by solving Eq. (6) for various values of the reduced anisotropy parameter  $d = -D/2Ng^2\beta^2(n_1-n_2)$ .

$d$	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80
$t_c$	0.333	0.362	0.385	0.404	0.419	0.432	0.443	0.452	0.459
$d$	0.90	1.00	1.10	1.30	1.50	1.70	2.00	2.50	$+\infty$
$t_c$	0.467	0.472	0.477	0.483	0.488	0.492	0.496	0.498	0.500

magnetic interaction to the interlayer antiferromagnetic interaction is equal to 6.6. An infinite value of this ratio would give rise to an infinite value of  $\chi_s$  and  $\chi_p$  at the Curie point.

Having made this choice of parameters, we have solved Eq. (5) for various values of  $T$  below the Curie point, using an iteration method and the G-20 computer. The numerical values obtained for  $M_0$  have been substituted into Eqs. (7) and (8), and the values of  $\chi_s$ ,  $\chi_p$ , and of the powder susceptibility  $\chi_p = \frac{1}{3}\chi_s + \frac{2}{3}\chi_p$  thus obtained below the Curie point have been plotted on Fig. 6.

#### COMPARISON BETWEEN THEORY AND EXPERIMENT IN THE CASE OF THE DIHYDRATE

The agreement between our experimental data for the dihydrate and our theoretical calculations for a metamagnet is fairly good (Fig. 6). The largest discrepancy happens in the case of  $\chi_a$  below 2°K. Our molecular-field theory predicts that  $\chi_s = \chi_a$  should vanish exponentially at low temperature, while our measurements indicate that  $\chi_a$  varies almost linearly in that range and that it might even have a small, positive, value at  $T=0$ . One should remember, however, that very small amounts of paramagnetic impurities in the sample or sample holder may increase the experimental susceptibility at very low temperatures. Secondly, the introduction of a small rhombic term into the spin Hamiltonian [Eq. (3)] would lead to a positive theoretical value of  $\chi_a$  at  $T=0$ , at the same time as it would explain the 5% difference observed between  $\chi_b$  and  $\chi_c$ ; our detailed calculations are only for uniaxial symmetry, as we feel that the slightly better agreement possible with a rhombic term does not justify at the present time the increased complication of the formulas, in the case of this salt.<sup>22</sup> Finally, we know that the molecular-field approximation is at best very rough at low temperatures, as it does not include the spin-wave collective excitations of the system, and it cannot be expected to give results in close agreement with the measurements in that range.

The most direct way of checking the simultaneous existence of strong ferromagnetic interactions and weaker antiferromagnetic interactions in nickel nitrate

dihydrate would be by observation of the transition to a simple ferromagnetic state which should take place<sup>16,17</sup> in a moderate magnetic field. Such measurements are planned for the future.

#### CONCLUSIONS

Our measurements of the powder susceptibility of nickel nitrate hexahydrate indicate that the crystal field acting on the  $S=1$  spins of the nickel ions is characterized by:  $E/k = -2.66^\circ\text{K}$ ;  $D/k = -8.67^\circ\text{K}$ ;  $g=2.25$ ; the same values are found in the case of the tetrahydrate. These values are obtained under the assumption that exchange interactions are negligible.

Nickel nitrate dihydrate undergoes a cooperative magnetic transition at 4.20°K. Our powder and single-crystal zero-field susceptibility measurements indicate that the ordered state below this temperature may be described by a two-sublattice model. Spins of the two different sublattices are aligned antiparallel by relatively weak antiferromagnetic exchange forces. Spins belonging to the same sublattice are brought to parallelism by stronger ferromagnetic forces. The results of a molecular field treatment of this  $S=1$  "metamagnet" are in fair agreement with the experimental data, assuming a value of 6.6 for the ratio of ferromagnetic to antiferromagnetic interactions. The existence of a one-ion anisotropy is assumed in these calculations, with  $D/k = -6.50^\circ\text{K}$ ;  $E/k \approx 0$ ;  $g=2.250$ . The  $a$  axis of the crystal is a preferred direction for the spins. The sublattices are probably layers parallel to the  $bc$  plane, according to direct structural evidence which shows strongest coupling between nickel ions belonging to the same  $bc$  sheet.

*Note added in proof.* V. Schmidt brought to our attention two determinations of the unit cell of nickel nitrate hexahydrate: A. Jayaraman, Proc. Indian Acad. Sci. **45A**, 263 (1957); D. Weigel, B. Imelik, and P. Laffitte, Bull. Soc. Chim. France, **29**, 544 (1962). The crystal is triclinic at room temperature, contrary to the old work by Marignac, reported in the book by Rammelsberg (see our Ref. 2).

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<sup>22</sup> One should also note that, due to the different directions of the anisotropy fields at the two types of nonequivalent nickel sites within a given  $bc$  layer, exchange interactions are not expected to lead to complete parallelism of the spins. This canting, which should result in a nonzero parallel susceptibility at zero temperature, is entirely neglected in the present paper.