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Low-Temperature Specific Heat of $Ni(NO_3)_2 \cdot 6H_2O$: Antiferromagnetic Interactions*

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Measurements of the specific heat of nickel nitrate hexahydrate for $0.5 < T < 12$ K reveal a Schottky anomaly with $C_{p\,\max} = 1.373$ cal/mole K at $T_{\max} = 2.35$ K. The experimental data are explained by the complete splitting of the $S = 1$ ground-state triplet, with levels separated successively by 4.80 and 3.26 K. The lattice contribution is found to be $4.11 \times 10^4 T^3$ cal/mole K. The discrepancies between the level spacings, as deduced from these measurements and the reported powder susceptibility data, are removed by taking into account a small antiferromagnetic exchange interaction ($A/k = +0.6$ K) in a molecular-field approximation. The total magnetic entropy change is found to be within 0.6% of the theoretically predicted value $R\ln 3$ for a spin-1 system.

INTRODUCTION

As part of a study of the magnetic behavior of Ni^{++} ions in certain hydrated salts, the susceptibility of powdered $Ni(NO_3)_2 \cdot 6H_2O$ was measured[1] in this laboratory down to 1.3 K. No cooperative phenomena were observed in those experiments. The data could be well described in terms of a conventional single-ion spin Hamiltonian for $S = 1$ with suitably chosen values of the axial and rhombic crystal-field parameters D and E and an isotropic splitting factor g. The zero-field splitting of the ground-state spin triplet deduced from the fitted values of D and E substantially exceeded kT at 1.3 K.

There remained, however, the interesting possibility that rather large exchange interactions might still exist among the Ni^{++} ions in $Ni(NO_3)_2 \cdot 6H_2O$. If their energy were small enough in comparison with the zero-field splitting of the ground-state triplet, then, as Moriya[2] has shown in a molecular-field approximation, no cooperative spin ordering transition would be detectable above 0 K. In the simple molecular-field picture, the presence of such "subcritical" interactions would be revealed through their contribution to the effective magnetic field at a Ni^{++} ion when an external field was applied. Thus, while both the low-field susceptibility and zero-field heat capacity of the system would appear in first approximation to be those of an assembly of noninteracting Ni^{++} ions, the single-ion parameters needed to fit the data would be the same only if the interactions were included in the calculation of the susceptibility. Such arguments have been invoked to explain apparent discrepancies in D and E deduced from thermal and magnetic observations on α-$NiSO_4 \cdot 6H_2O$[3-5] and $Ni(CH_3COO)_2 \cdot 4H_2O$.[6]

Heat capacity measurements on $Ni(NO_3)_2 \cdot 6H_2O$ were undertaken to obtain estimates of D and E independent of the earlier magnetic results[1] and to detect any subcritical spin interactions that might exist. As will be seen, the analysis of the data does admit the inclusion of a small molecular-field term of antiferromagnetic sign.

EXPERIMENTAL

The experiments reported here were carried out in two completely separate experimental apparatuses. For $0.5 < T < 4.2$ K a standard liquid-^{3}He-cooled adiabatic calorimeter was used (apparatus I). It has been described elsewhere.[7] The sample was cooled to low temperatures by means of a mechanical heat switch. The region above ~1.7 K was covered by a similar ^{4}He calorimeter (apparatus II), which used exchange gas in cooling down the sample.

The sample holders were copper capsules each carrying a manganin electrical heater and a resistance thermometer. A germanium thermometer[8] and a carbon composition resistor[9] were used in I and II, respectively.

Calibrations of the thermometers were performed against the saturated vapor pressures of ^{3}He (0.4–1.6 K),[10] ^{4}He(1.1–4.2 K),[11] and H_2 (13.9–19.8 K).[12] The calibration data were fitted to a polynomial of the form $[\ln(R)/T]^{1/2} = \sum_n A_n \ln^n(R)$. The standard deviation of the fit with $n = 3$ for the 27 data points in the range 0.4–4.2 K (Ge thermometer) was 1%. For the carbon resistor, the interpolation between 4.2 and 13.9 K was based on 28 calibration points in the range 1.7–4.2 K and 22 points in the range 13.9–19.8 K. The standard deviation of the fit with $n = 6$ was 0.06%.

The resistance of the thermometers was measured with an ac Wheatstone bridge, incorporating a lock-in amplifier as the null detector.

A discontinuous heating technique was employed for the specific-heat measurements, i.e., the temperature increase of sample plus addenda was measured upon an accurately known heat input. The

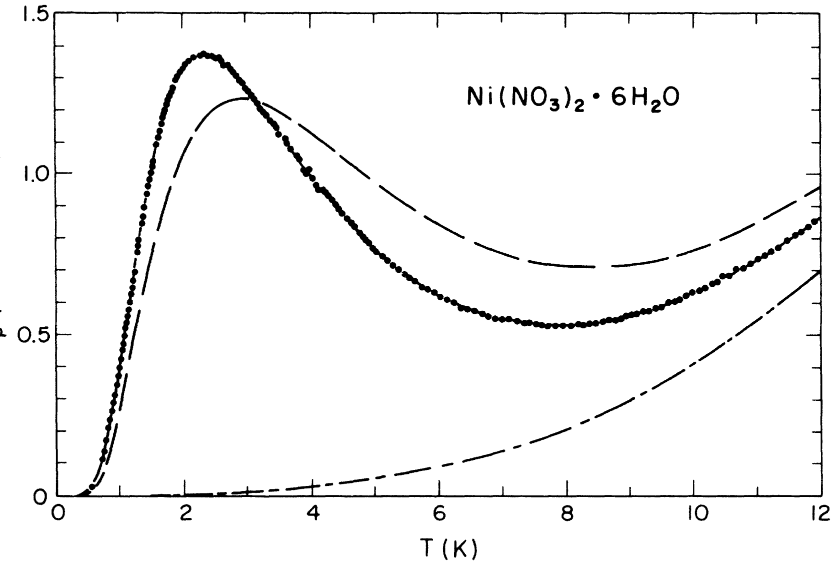

FIG. 1. Specific heat of nickel nitrate hexahydrate as a function of temperature. Full line: theoretical curve for an $S=1$ paramagnet [formula (2), with $D/k=+6.43$ K, $E/k=+1.63$ K] plus a lattice contribution $C_{\text{lat}}=4.11\times10^{-4}\ T^3$ cal/mole K. Dashed line: same, but with $D/k=+8.33$ K, $E/k=+3.00$ K. The lattice contribution is shown separately by the dot-dashed line.

heat capacities of the empty capsules were measured in separate runs. Their contributions to the total heat capacity amounted to about 4% at 4 K and 20% at 12 K.

The samples used for this research were recrystallized at 30 °C by evaporation from a saturated aqueous solution of Baker Analyzed Reagent grade material. The crystals had an average linear dimension of ca. 2 mm. About 20 g were sealed in the capsules, together with a small amount of ^{3}He or ^{4}He exchange gas (3.5 Torr at 77 K). Care was taken to protect the sample from dehydration during the capsule filling procedure by cooling it to 77 K.

RESULTS AND DISCUSSION

The experimental results in the range 0.5–12 K are plotted in Fig. 1 and summarized in Table I. The data given for $T<4.2$ K are those obtained with apparatus I. Of the data taken with apparatus II, we present only those values for $T>4.2$ K. The two sets of data match smoothly from 3.5 to 4.5 K. Small systematic discrepancies between the two sets below 3.5 K (amounting to a few percent at 2.4 K) are traceable to experimental difficulties arising from the use of exchange gas in apparatus II and apparent dehydration of one of the samples. The results given here for $T<4.2$ K have been reproduced in three separate experimental runs.

The specific heat is seen to pass through a relatively broad maximum at 2.35 K, indicative of the Schottky anomaly associated with the gradual population of the upper two spin components of the Ni^{++}-ion ground state with increasing temperature.

In the absence of exchange interactions, the spin Hamiltonian for a single nickel ion in an octahedral crystal field with axial and rhombic distortions is[13]

$$\mathcal{H}=DS_z^2+E(S_x^2-S_y^2)+g\mu_B\vec{S}\cdot\vec{H}\ . \qquad (1)$$

Defining D and E as positive numbers and taking $S=1$ for the effective spin of the Ni^{++} ion, the energy eigenvalues of (1) for $\vec{H}=0$ are 0, $(D-E)$, and $(D+E)$, with the zero level lowest. The expression for the specific heat of a system of N free nickel ions in zero field can be derived from the partition function for this level scheme, $Z=1+e^{-(D-E)/kT}+e^{-(D+E)/kT}$, using the relation

$$C=\frac{\partial}{\partial T}\left(NkT^2\ \frac{\partial \ln Z}{\partial T}\right)\ . \qquad (2)$$

On the assumption that the lattice contribution to the specific heat obeys Debye's T^3 law in the temperature range of interest and that it is separable from the magnetic contribution, the total specific heat can be represented by

$$C_p=\beta T^3+C_{\text{mag}}\ , \qquad (3)$$

where β is a constant and C_{mag} is given by (2).

Using a function minimization procedure developed by Fletcher and Powell[14] we have fitted the experimental data to relation (3). Adjusting $(D-E)$ and $(D+E)$ to minimize the function $\sum_i(C_{i\,\text{expt}}-C_{i\,\text{calc}})^2$, where C_i is the total specific heat at temperature T_i, we found

$$\beta=4.11\times10^{-4}\ \text{cal/mole K}^4,$$
$$D/k=+6.43\ \text{K}, \qquad (4)$$
$$E/k=+1.63\ \text{K}\ .$$

The curve for C_{calc} obtained by substituting these values into (3) and (2) is shown as a full line in Fig. 1 and it is seen to represent the data very well. The standard deviation of the fit is 0.7%.

The assumption that the Ni^{++}-ion ground state in this salt is actually a triplet ($S=1$) is further supported by entropy considerations. Correcting the C_p data for the lattice contribution and using the theoretical expression (with D and E as given above) to extrapolate C_{mag} from 0.5 to 0 K and from 12 K to ∞, one may calculate the entropy difference between the state in which all three components of

TABLE I. Heat capacity of $Ni(NO_3)_2 \cdot 6H_2O$. C_p is given in cal/mole K and T in Kelvins.

T	C_p	T	C_p	T	C_p	T	C_p
0.551	0.028	1.981	1.318	4.632	0.848	9.306	0.577
0.717	0.114	2.005	1.324	4.700	0.832	9.404	0.585
0.748	0.139	2.052	1.342	4.711	0.815	9.506	0.589
0.779	0.171	2.105	1.350	4.831	0.803	9.610	0.601
0.822	0.211	2.177	1.365	4.873	0.796	9.718	0.607
0.848	0.234	0.280	1.367	4.913	0.786	9.792	0.612
0.872	0.262	2.354	1.373	4.997	0.768	9.894	0.622
0.896	0.288	2.416	1.365	5.040	0.760	9.987	0.631
0.922	0.315	2.482	1.364	5.130	0.742	10.113	0.638
0.951	0.346	2.529	1.360	5.208	0.730	10.191	0.648
0.973	0.372	2.580	1.362	5.291	0.716	10.294	0.659
0.994	0.400	2.622	1.351	5.379	0.702	10.398	0.664
1.015	0.426	2.664	1.339	5.472	0.690	10.470	0.681
1.035	0.452	2.730	1.340	5.565	0.675	10.571	0.684
1.053	0.473	2.753	1.330	5.643	0.666	10.684	0.705
1.072	0.492	2.801	1.314	5.758	0.650	10.794	0.705
1.090	0.522	2.852	1.305	5.847	0.641	11.007	0.734
1.123	0.560	2.911	1.290	5.940	0.630	11.120	0.745
1.139	0.578	2.956	1.284	6.038	0.620	11.234	0.760
1.157	0.600	3.003	1.265	6.142	0.609	11.352	0.770
1.175	0.624	3.049	1.260	6.252	0.600	11.474	0.799
1.192	0.645	3.096	1.242	6.361	0.583	11.594	0.811
1.209	0.668	3.143	1.230	6.460	0.580	11.697	0.818
1.227	0.692	3.189	1.220	6.568	0.576	11.802	0.836
1.278	0.753	3.237	1.202	6.682	0.568	11.910	0.852
1.296	0.776	3.288	1.193	6.797	0.557		
1.315	0.792	3.337	1.183	6.898	0.555		
1.354	0.846	3.391	1.166	7.004	0.550		
1.375	0.867	3.448	1.154	7.116	0.547		
1.396	0.895	3.477	1.144	7.233	0.542		
1.436	0.936	3.507	1.120	7.348	0.538		
1.456	0.961	3.600	1.112	7.430	0.537		
1.476	0.981	3.629	1.095	7.522	0.534		
1.496	1.002	3.690	1.079	7.617	0.533		
1.516	1.024	3.778	1.058	7.727	0.528		
1.537	1.038	3.838	1.047	7.839	0.528		
1.580	1.090	3.890	1.009	7.957	0.530		
1.620	1.115	3.946	0.999	8.081	0.532		
1.639	1.132	3.975	1.017	8.200	0.534		
1.659	1.157	4.028	0.987	8.291	0.532		
1.693	1.177	4.080	0.964	8.383	0.536		
1.710	1.188	4.135	0.951	8.479	0.539		
1.726	1.199	4.191	0.947	8.579	0.543		
1.746	1.217	4.247	0.941	8.681	0.546		
1.767	1.230	4.294	0.931	8.775	0.547		
1.787	1.242	4.344	0.916	8.857	0.552		
1.828	1.259	4.396	0.903	8.942	0.561		
1.854	1.268	4.451	0.890	9.029	0.564		
1.886	1.290	4.508	0.875	9.119	0.565		
1.916	1.301	4.569	0.861	9.211	0.573		

the triplet are equally populated and the state in which the lowest is exclusively populated. This entropy difference is found to be within 0.6% of the theoretical value $R\ln 3$. The extrapolated contributions amount to about 5% of the total.

Also shown in Fig. 1 is the curve for C_{calc} obtained with the same lattice coefficient but with the D and E values derived from the powder susceptibility results,[1] assuming the Ni^{++} ions to be noninteracting ($D/k = +8.33$ K, $E/k = +3.00$ K). Large systematic discrepancies, far outside the limits of experimental error, exist between this curve and the experimental data. They suggest that subcritical interactions, as defined earlier, exist in $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and must be included in a consistent analysis of the magnetic and thermal data.

In the molecular-field approximation, one replaces the sum of the isotropic exchange interactions of the ith Ni^{++} ion with z nearest neighbors (assumed equivalent) by the expression $A\vec{S}\cdot\langle\vec{S}\rangle$, where $A = -zJ$ and $\langle\vec{S}\rangle$ is the expectation value of the spin thermally averaged over the three components of the ground state. When added to the single-ion Hamiltonian [Eq. (1)], this contribution may be combined with the Zeeman term $g\mu_B\vec{S}\cdot\vec{H}$ if we replace the field $\vec{H}$ by an effective field $\vec{H}+A\langle\vec{S}\rangle/g\mu_B$. When $\vec{H}=0$, as in the present heat capacity experiments, $\langle\vec{S}\rangle = 0$ at all temperatures and the zero-field eigenvalues of Eq. (1) and the simple partition function given above should be used to fit the data. The results are those already given in Eqs. 4. Since even the initial magnetic susceptibility is measured with $\vec{H}\neq 0$, for which $\langle\vec{S}\rangle \neq 0$, we must use the full Hamiltonian, including the Zeeman and molecular-field terms, in calculating the appropriate theoretical expression. One finds for the powder susceptibility

$$\chi_{\text{powder}} = \frac{2Ng^2\mu_B^2}{3}\left(\frac{Z_2}{(D+E)Z_1+2AZ_2} + \frac{Z_3}{2EZ_1+2AZ_3} + \frac{Z_4}{(D-E)Z_1+2AZ_4}\right), \qquad (5)$$

where

$$Z_1 = 1 + e^{-(D-E)/kT} + e^{-(D+E)/kT},$$

$$Z_2 = 1 - e^{-(D+E)/kT},$$

$$Z_3 = e^{-(D-E)/kT} - e^{-(D+E)/kT},$$

$$Z_4 = 1 - e^{-(D-E)/kT}.$$

The χ_{powder} data from Ref. 1 have been plotted in Fig. 2. Using Eq. (5) with the values for D and E obtained from the analysis of the C_p results ($D/k = +6.43$ K, $E/k = +1.63$ K) and with $g = 2.25$, the values for A/k required to fit the data points below 4 K range from $+0.60$ to $+0.64$ K (antiferromagnetic sign).

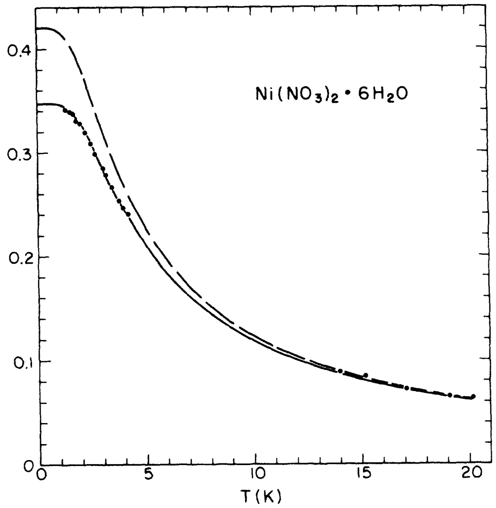

FIG. 2. Powder susceptibility of nickel nitrate hexahydrate as a function of temperature. Full line: theoretical curve [formula (5), with $g = 2.25$, $D/k = +6.43$ K, $E/k = +1.63$ K, and $A/k = +0.62$ K]. Dashed line: same, but with $A = 0$. Data points are taken from Ref. 1.

The calculated values of A for the data in the hydrogen region alone exhibit considerable scatter in both magnitude and sign. This result is not particularly surprising considering the fact that attempts to determine the value of a necessarily small[2] molecular-field constant from data taken at temperatures such that $kT \approx 25A$ require extremely accurate data. Even if such observations were available, it is more reasonable to use data with kT on the order of the interaction energy. This is illustrated in Fig. 2; the full line gives the theoretical prediction (5) using $D/k = +6.43$ K, $E/k = +1.63$ K, $g = 2.25$, and $A/k = +0.62$ K. The dashed line is the curve predicted for these values of D, E, and g but with $A = 0$. It is to be noted that the full line in Fig. 2 agrees to within 1% with the curve of Fig. 4 in Ref. 1, which gives the best fit to the data points assuming A to be identically zero.

Similar magnetic behavior has been reported for α-$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. Using Watanabe's χ_{powder} data in the helium range[3] and crystal-field parameters derived from their own specific-heat measurements, Stout and Hadley[4] concluded that subcritical ferromagnetic interactions were present in this substance, with $-0.7 < A/k < -0.1$ K.

We feel that the values $D/k = +6.43$ K, $E/k = +1.63$ K, $A/k = +0.6$ K, $g = 2.25$, and $C_{\text{lat}}/T^3 = 4.11 \times 10^{-4}$ cal/mole K^4 successfully describe the available low-temperature thermal and magnetic data on $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The estimated interaction constant A satisfies the inequality $A < \frac{1}{2}|D-E|$ and consequently, according to Moriya's analysis, is too small to produce long-range magnetic order at a nonzero temperature. This picture could be significantly altered at quite low temperatures if it were possible to apply a suitably oriented magnetic field of sufficient magnitude to give each Ni^{++} ion a substantial magnetic moment. The interesting possibility of observing long-range ordering of such induced moments depends critically on the structure of the salt which, unfortunately, is not yet known in detail.[15] We are unable, at present, to predict whether or not such effects should be observable. While A appears to be large in comparison with typically dipolar interaction energies, accurate estimates of the relative importance of exchange and dipolar coupling in $Ni(NO_3)_2 \cdot 6H_2O$ must also await the full determination of its structure. Further magnetic and thermal studies of single crystals of this substance at very low temperatures are being undertaken.

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Extra-Orbital Model of a Dilute Metallic Alloy*

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Accurate values of both localized and conduction-band quasiparticle excitation energies are calculated for the extra-orbital model of a dilute metallic alloy. It is shown that this model can always be made self-consistent in the sense of satisfying the Friedel sum rule.

I. INTRODUCTION

In recent years, the most intensively studied model of a metallic alloy has been the so-called single-site approximation.[1, 2] Here we wish to discuss a somewhat different model, one particularly appropriate where the minority constituents of the alloy are transition elements. We approximate the effect of each impurity atom by that of an *extra orbital*, coupled to the conduction band of the host metal. As Velický *et al.*[2] have pointed out, the single-site approximation is related to the many-electron Hubbard model[3] of a narrow-band solid. Similarly, the extra-orbital approximation is related to the many-electron Anderson model[4] of a localized magnetic center in a metal.

In this paper we restrict the discussion to a dilute alloy containing a single type of impurity element. We use the operator equation-of-motion method[5] to find accurate values for both localized and conduction-band quasiparticle excitation energies. Just as Stern[6] has done recently for the single-site