

Measurement of the Nuclear and Electronic Contributions to the Specific Heat of Neodymium Ethyl Sulfate near 1°K

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The molar specific heat C_I of neodymium ethyl sulfate has been measured on three samples of separated neodymium isotopes in the temperature range 0.95°K – 2.15°K by the magnetic method of Benzie and Cooke at frequencies from 300 to 1200 cps. The measured C_I may be described within 1 percent by $C_I = b/T^2$, where T is the temperature and b is the constant. All three samples were shown by x-ray diffraction measurements to have the same structure as that given for neodymium ethyl sulfate by Ketelaar. For the electron contribution to the specific heat we obtained $b_e = 0.146 \pm 0.004 \times 10^6$, and for the hyperfine splitting contributions we obtained $b_{143} = 5.08 \pm 0.05 \times 10^6$ and $b_{145} = 1.7 \pm 0.2 \times 10^6$ erg degree. These values of b_{143} and b_{145} agree within experimental error with the corresponding values computed from the microwave measurements of Scovil. Thus, the hyperfine splitting contribution to the specific heat for $\text{Nd}^{143}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ is some 35 times larger than the electron contribution which makes this material of interest for the study of nuclear effects below 1°K .

INTRODUCTION

IT has been suggested by H. B. G. Casimir¹ and by C. J. Gorter² that the properties of magnetically dilute paramagnetic salts (excluding lattice effects) can be described in terms of a parameter b/C the ratio of the specific heat constant b to the Curie constant C . Here, b is given by the equation $C_I = b/T^2$, with C_I the molar specific heat at constant magnetization and T the absolute temperature.

In this paper, we show that $b = b_e + b_n$, where b_e is produced by the electron dipole-dipole and exchange interaction contribution to the specific heat, and b_n arises from the electron nuclear interaction. Because of this linear contribution of b_n to b , it is possible to measure b for several samples of different isotopic composition and separate the nuclear contribution. This new procedure differs from the dilution technique³ of measuring the nuclear contribution to the specific heat in that extrapolation to infinite dilution is unnecessary and assumptions regarding the linearity of b_e as a function of dilution do not enter. Thus it is possible to measure a small b_e in the presence of a large b_n .

The parameter b/C has been measured for three samples of neodymium ethyl sulfate $\text{Nd}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ in the temperature region near 1°K . Sample I was prepared from neodymium of normal isotopic composition, sample II was prepared from neodymium highly enriched in Nd^{142} , and in sample III the neodymium was highly enriched in Nd^{143} . When the measured values of b/C for each of the three samples were multiplied by the Curie constant C , the respective specific heat constants b were obtained. Collecting these values of b in

three simultaneous equations, we have calculated the electron spin interaction contribution to the specific heat b_e/T^2 and the hyperfine splitting contribution to the specific heat b_n/T^2 , for both Nd^{143} and Nd^{145} .

THEORY

Following Casimir¹, Gorter,² and Benzie and Cooke⁴ we may obtain the specific heat from purely magnetic measurements. It is given by

$$C_I = \frac{CT}{(T-\theta)^3} \frac{\chi_s}{\chi_T - \chi_s} H^2, \quad (1)$$

where θ is the Weiss constant, χ_T and χ_s are the isothermal and adiabatic differential magnetic susceptibilities, respectively, and H is an applied constant magnetic field. The above H is applied parallel to the relatively small alternating field used to measure the susceptibilities. At zero magnetic field, $\chi_T = \chi_s$; and when a field is applied, χ_T remains constant within a small saturation correction.⁴ On the other hand, χ_s is, in general, a function of the magnetic field, the specific heat resulting from electron-spin interactions, the electron spin-lattice relaxation time, the specific heat of the lattice along with the sample surroundings, and their thermal conductivities.⁵ When χ_s is measured at sufficiently high frequencies, relaxation time and thermal conductivity effects can be made negligible. In these experiments, the reactive component of the susceptibility χ_s' was shown experimentally to be independent of the frequency within approximately one percent in the range from 300 to 1200 cycles per second. This is taken as sufficient evidence that χ_s' varies with H , T , and C_I only, in this frequency range, and that the

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¹ H. B. G. Casimir, *Magnetism and Very Low Temperatures* (Cambridge University Press, Cambridge, 1940).

² C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Amsterdam, Netherlands, 1947).

³ R. J. Benzie and A. H. Cooke, *Nature* **164**, 837 (1949).

⁴ R. J. Benzie and A. H. Cooke, *Proc. Phys. Soc. (London)* **A63**, 213 (1950).

⁵ J. Eisenstein, *Phys. Rev.* **84**, 548 (1951).

measured χ_s' is the χ_s of Eq. (1). Assuming that the specific heat from about 1°K to 2°K may be described by

$$C_I = b/T^2, \quad (2)$$

we find that Eq. (1) reduces to

$$\frac{b}{C} = \frac{T^3}{(T-\theta)^3} \frac{\chi_s}{\chi_T - \chi_s} H^2. \quad (3)$$

Equation (3) was used to calculate θ and b/C from our measured values of H , T , χ_s , and χ_T .

To demonstrate that $b = b_e + b_n$, we begin with the partition function z

$$z = \text{Tr} e^{-\mathcal{H}/kT},$$

where \mathcal{H} is the Hamiltonian describing the salt and k is the Boltzmann constant. The specific heat is then given by

$$C_I = T \frac{\partial S}{\partial T} = NkT \frac{\partial^2 T \ln z}{\partial T^2},$$

where N is Avogadro's number. Expanding z to second order in $\text{Tr} \mathcal{H}/kT$, we find

$$C_I = Nk \frac{1}{k^2 T^2} \frac{\text{Tr} \mathcal{H}^2}{(2S+1)(2I+1)}. \quad (4)$$

Here S and I are the electron and nuclear spins.

The Hamiltonian for $\text{Nd}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ at liquid He temperatures is

$$\mathcal{H} = AI_x S_x + B(I_y S_y + I_z S_z) + P(S). \quad (5)$$

The first two terms on the right are the contribution to the Hamiltonian produced by the asymmetrical hyperfine coupling as given by Bleaney and Scovil,⁶ and the third term $P(S)$ corresponds to the electron dipole-dipole and exchange interactions as discussed by Van Vleck.⁷

Since $\text{Tr} I = 0$, there are no cross terms, and $\text{Tr} \mathcal{H}^2$ reduces to

$$\text{Tr} \mathcal{H}^2 = \text{Tr} [AI_x S_x + B(I_y S_y + I_z S_z)]^2 + \text{Tr} P^2(S). \quad (6)$$

TABLE I. Isotopic composition of the neodymium used to prepare the samples.

Isotope	Sample I	Percent abundance		Sample III
		Sample I	Sample II	
142	27.13	93.00	4.04	
143	12.20	3.18	83.93	
144	23.87	2.89	8.83	
145	8.30	0.368	1.78	
146	17.18	0.414	1.16	
148	5.72	0.084	0.149	
150	5.60	0.066	0.108	

⁶ B. Bleaney and H. E. D. Scovil, Proc. Phys. Soc. (London) **A63**, 1369 (1950).

⁷ J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937).

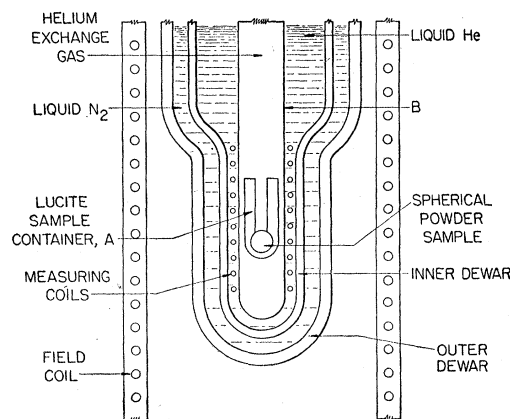


FIG. 1. Apparatus.

Thus, the specific heat is

$$C_I = \frac{b}{T^2} = \frac{(b_n + b_e)}{T^2}, \quad (7)$$

where

$$b_e = \frac{N}{k} \frac{\text{Tr} P^2(S)}{(2S+1)(2I+1)}, \quad (8)$$

$$b_n = \frac{N}{k} \frac{\text{Tr} [AI_x S_x + B(I_y S_y + I_z S_z)]^2}{(2S+1)(2I+1)}. \quad (9)$$

The latter trace from Bleaney,⁸ gives

$$b_n = \left[\frac{1}{3}\right] (A^2 + 2B^2) \cdot S(S+1)I(I+1)Nk.$$

Thus, since there are no cross terms, the traces Eqs. (8) and (9) and, hence, b_e and b_n are independent of the isotopic composition of the paramagnetic salt. For a given isotopic composition of paramagnetic ions, one may write the equation

$$b = b_e + \sum_i F_i b_{ni}, \quad (10)$$

where F_i is the fraction of the i th paramagnetic isotope present and b_{ni} is the corresponding nuclear specific heat constant. By measuring b for a series of salts having different isotopic compositions, one may solve the corresponding set of simultaneous equations for b_e and for the b_{ni} of each isotope.

EXPERIMENTAL PROCEDURE

The normal neodymium ethyl sulfate, sample I, was prepared by D. E. LaValle of this laboratory from neodymium oxide which was spectroscopically pure. The neodymium isotopic composition of this sample was assumed to be that given by J. Mattauch⁹ and co-workers.

The neodymium ethyl sulfate samples II and III were prepared by R. H. Sampley of this laboratory using

⁸ B. Bleaney, Phys. Rev. **78**, 214 (1950).

⁹ J. Mattauch and V. Hauk, Naturwiss. **25**, 781 (1937).

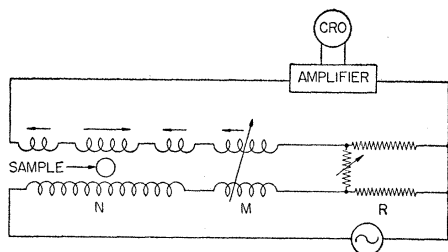


FIG. 2. Electrical circuit.

the oxides enriched in Nd^{142} and Nd^{143} , respectively. These oxides were also of spectroscopic purity. The isotope separation and mass analyses of samples II and III were performed by the Stable Isotopes Division of this laboratory. Their results for the mass analyses are tabulated in Table I.

Each of the three samples of the salt was identified by x-ray diffraction methods. A single crystal (approximately 0.1 mm in diameter) was mounted by means of grease on a glass fiber. A Weissberg goniometer was used to take a rotation photograph and zero and first-layer Weissberg photographs. From these data the three samples were found to be identical and to be hexagonal, with $a=14.02$ Å, $c=7.12$ Å, and $c/a=0.5078$. This compares favorably with the optical measurements of Singh,¹⁰ who reported $\text{Nd}(\text{C}_2\text{H}_3\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ to be hexagonal with $c/a=0.5075$, and with the x-ray measurements of Ketelaar,¹¹ who reported $a=13.992$, $c=7.07$, and $c/a=0.505$.

Each of the three samples was recrystallized three times. The last recrystallization in each case was performed immediately before the low temperature measurements were made.

Each sample contained approximately one gram of small crystals of the salt (about 0.1 mm³ average size) which were compressed into a spherical Lucite container A (Fig. 1) of 12.7 mm internal diameter. The compression was to about 80 percent of the crystal density. Container A was inserted into a glass tube B. This tube was immersed in liquid helium which was in turn contained in a Dewar flask jacketed in liquid nitrogen. Thermal contact between the sample in A and the liquid helium which surrounded tube B was maintained by helium gas at a pressure of about 50 microns Hg.

The susceptibilities χ_s and χ_T of the sample salt were measured by a compensated mutual-inductance (Hartshorn) bridge as described by de Klerk.¹² The electrical circuit is shown schematically in Fig. 2. The sample was placed in a mutual inductance N (Fig. 2) in the cryostat. Its susceptibility in arbitrary units was given in terms of the setting of the variable mutual inductance M required to balance the contribution of the sample to the mutual inductance. The loss component of the susceptibility was balanced by the resistance net R .

The secondary winding of the mutual inductance N was divided into three sections. The central section of 2441 turns was opposed by two end sections of $1220\frac{1}{2}$ turns each. The sample was carefully positioned at the center of the middle section. The primary coil of N , of 298 turns per cm, produced an alternating field of approximately seven gauss at the sample.

To obtain the adiabatic susceptibility, a steady magnetic field ($0 < H < 1000$ gauss) was applied to the sample by an iron-free oil-cooled solenoid fed by storage batteries. The field current was measured by a standard shunt and a type K potentiometer. The field was calibrated by both the standard mutual inductance and the proton resonance methods with good agreement. The accuracy of every field measurement was to within $\frac{1}{2}$ percent.

Above 1.1°K the temperature of the sample was determined by measuring the vapor pressure over the surrounding liquid-helium bath and converting to temperature by the Royal Society Mond Laboratory Tables of June, 1949. This pressure was regulated by adjusting a suitable valve in the pumping line. Below 1.1°K the temperature was obtained from the sample susceptibility.

RESULTS

Measurements of the parameter b/C were made at 300, 600, 900, and 1200 cycles per sec at a number of temperatures (Table II), and the value listed for a given temperature is the average result for these four frequencies with an average deviation of less than 1 percent.

The value for the specific heat constant b for each of the three samples was obtained by multiplying the average value of b/C for the several temperatures by the Curie constant per mole. The latter constant $C=0.663$ for the powder sample was calculated both from microwave measurements by Scovil¹³ and from the suscepti-

TABLE II. Measurements of b/C on three neodymium samples.

T (°K)	Sample I	$b/C \times 10^{-5}$ Sample II	Sample III
2.155			6.81
2.150		0.481	
2.145	1.363		
1.640		0.476	
1.630			6.62
1.450			6.64
1.390		0.466	
1.122	1.361		
1.121			6.70
1.103		0.477	
1.000	1.377		
0.970		0.472	
0.950			6.72
Average	1.367	0.474	6.70
Weiss $\theta=0.013 \pm 0.005^\circ\text{K}$			

^a Average value for 300, 600, 900, and 1200 cps.

¹⁰ Von Sohan Singh, *Z. Krist.* **105**, 384 (1944).

¹¹ J. A. A. Ketelaar, *Physica* **4**, 619 (1937).

¹² D. de Klerk, thesis, Leiden, 1948.

¹³ H. E. D. Scovil, *Proceedings of the International Conference on Low Temperature Physics*, R. Bowers, editor (Clarendon Laboratory, Oxford, 1951), p. 150.

bility measurements of Van den Handel and Hupse¹⁴ with excellent agreement. For sample I, the normal neodymium sample, $b_I = 0.906 \times 10^5$ erg deg; for sample II, $b_{II} = 0.314 \times 10^5$ erg deg; and for sample III, $b_{III} = 4.44 \times 10^5$ erg deg. Collecting these values of b in the corresponding simultaneous equations, we then found it possible to solve for the three contributions of the specific heat: b_e , the specific heat constant b_{143} corresponding to the Nd^{143} hyperfine splitting, and the specific heat constant b_{145} corresponding to the Nd^{145} hyperfine splitting. These equations and the values of b_e , b_{143} , and b_{145} are given in Table III.

The values of b given in Table III are to be compared with the values $b_{143} = 5.17 \times 10^5$ erg deg and $b_{145} = 2.00 \times 10^5$ erg deg computed from the microwave measurements of Scovil.¹³ Because of the small percentage of Nd^{145} in the three samples, the experimental error of our b_{145} measurement is relatively large. This value of $b_e = 0.146 \pm 0.004 \times 10^5$ is one of the smallest electron-electron interactions that has been observed, and this smallness is consistent with the fact that in his microwave measurements Bleaney⁶ was able to resolve the hyperfine structure on the undiluted salt. This results in the unusual circumstance that for $\text{Nd}^{143}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ the hyperfine splitting contribution to the specific heat is some 35 times larger than the electron-electron interaction contribution, which makes this material of interest in the study of nuclear effects below 1°K.

In Table II a Weiss constant of $0.013 \pm 0.005^\circ\text{K}$ was used in calculating the specific heat. This value is smaller than can be obtained precisely from susceptibility measurements. Our value of b_{143} without a Weiss constant correction was approximately 4 percent lower than the corresponding microwave value. In that the precision of our susceptibility and magnetic field measurements was considerably better than 1 percent, it is reasonable to assume that the above 4 percent discrepancy is produced by a small Weiss constant, and the above value of θ is that which is necessary to bring our b_{143} value into agreement with the microwave results within our experimental error. Since θ can be shown to be independent of the isotopic composition, the value determined above applies to all three samples.

This comparison provides a very sensitive technique for observing a Weiss constant in that the Weiss constant enters into the specific heat measurement to the third power, whereas it only enters linearly in susceptibility measurements.

This θ of 0.013°K leads to a b (exchange) which is small compared to our measured value for b_e . This

¹⁴ J. Van den Handel and J. C. Hupse, *Physica* 9, 223 (1942).

TABLE III. Simultaneous equations for specific heats of neodymium samples.

$4.44 \times 10^5 = b_e + 0.8393b_{143} + 0.0178b_{145}$
$0.906 \times 10^5 = b_e + 0.1220b_{143} + 0.0830b_{145}$
$0.314 \times 10^5 = b_e + 0.0318b_{143} + 0.0037b_{145}$
$b_{143} = 5.08 \pm 0.05 \times 10^5$ erg deg
$b_{145} = 1.7 \pm 0.2 \times 10^5$ erg deg
$b_e = 0.146 \pm 0.004 \times 10^5$ erg deg

suggests that b_e for these salts is predominantly the result of dipole-dipole interaction.

APPLICATION OF THIS TECHNIQUE TO TRIVALENT URANIUM

Experiments are in progress applying the above separated isotope technique to the measurement of the nuclear specific heat of trivalent uranium. The only stable compounds of trivalent uranium are the halides; and, as these become antiferromagnetic at about 350°K, according to Dawson,¹⁵ they are unsuitable for these measurements. Since the uranium trihalides are isomorphous with the lanthanum trihalides, it is possible to prepare solid solutions of these. Because of the low symmetry of the crystal, and because UX_3 has an odd number of electrons, solid solutions dilute in uranium may be expected to have a Kramers doublet as the ground state and thus be paramagnetic in the liquid helium temperature region. We have prepared a number of $\text{UF}_3\text{-LaCl}_3$ and $\text{UCl}_3\text{-LaCl}_3$ samples with uranium molar volumes in the range from 600 cc to 3000 cc. All of these, when freshly prepared, are found to follow a Curie law in the temperature region from 1°K–4°K. The Curie constant for the powder is of the order of magnitude to be expected for a Kramers doublet and an average spectroscopic splitting factor g of the order of 2. This g is probably anisotropic, so single crystal measurements would be necessary to obtain complete information about it. The more dilute of these normal uranium solid solutions have been cooled by adiabatic demagnetization from 1.17° to about 0.7° using initial magnetic fields of about 5000 gauss.

Note added in proof.—Professor R. J. Elliott has calculated the b_e to be expected from dipole-dipole interaction for $\text{Nd}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ and obtains the value $b_e = 0.144 \times 10^5$ erg degree. This is to be compared with our experimental value, $b_e = 0.146 \times 10^5$. The good agreement between these values indicates that the electronic contribution to the specific heat is almost entirely due to dipole-dipole interaction.

¹⁵ J. K. Dawson, Harwell, AERE Report C/R 578, September, 1950.