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Low Temperature Magnetic Properties and Antiferromagnetic Interactions of the Magnetic Susceptibility Calibrant $HgCo(NCS)_4$

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High sensitivity magnetic susceptibility determinations in the range 1.3–100K, on $HgCo(NCS)_4$*, a common susceptibility calibrant, are reported. Earlier literature data reported for calibration purposes are shown to be inaccurate. Previously undetected antiferromagnetic interactions are shown to exist in* $HgCo(NCS)_4$*, causing deviation from Curie–Weiss behavior at low temperatures.*

Introduction

The salt mercury cobalt thiocyanate, $HgCo(NCS)_4$, is widely used as a calibrant for magnetic susceptibility measurements at high temperatures [1–4]. Its suitability as a calibrant is also mentioned by manufacturers of commercial apparatus for high sensitivity magnetic susceptibility measurements [5, 6]. Accurate susceptibility data are therefore important. The magnetic properties have been carefully [2] measured at 25 °C, where $\chi_g = 16.44 \times 10^{-6}$ cgsemu. The temperature dependence of the susceptibility has been examined over the range 80–300K [3] and separately over 5.6–293K to make the salt useful for calibrations at low temperatures [4]. The two data sets disagree significantly over most of the overlapping temperature region, and we were unable to make calibration data from $HgCo(NCS)_4$ agree with those obtained from other calibrants. We have therefore made a detailed examination of the magnetic properties in the range 1–100K, with emphasis on precision and reproducibility of susceptibility and (particularly) temperature measurements. Less accurate measurements in the range 5–300K were made using a different experimental technique to provide an independent check of the results.

After completion of our study, a third investigation of the temperature dependence of the susceptibility of $HgCo(NCS)_4$ was reported [7]. This data disagrees with the previous two data sets, though the existence of antiferromagnetic interactions, which we report here, was overlooked in all the studies.

Experimental

Magnetic susceptibilities in the range 4–100K were recorded on a SQUID magnetometer [5, 8], which is capable of obtaining very high sensitivity absolute susceptibility measurements. The measuring SQUID was calibrated by passing a current through an inductance coil, calculating the change in flux quanta, and observing the change in the digital voltmeter coupled to the SQUID. The susceptibility, χ_g, is determined from the change in the number of flux quanta ($\Delta\phi$) at a fixed magnetic field (H) in the coils of a superconducting magnet. Thus, for a sample of uniform cross-section, length l and mass m,

$$\chi_g = \frac{\Delta\phi l}{4\pi Hm} .$$

Temperature determinations were made using silicon diode, germanium diode, helium vapor and carbon resistor thermometers, and further checks of temperature were based on the susceptibilities of two manganese(II) salts [9, 10] as described below, and the superconducting transition temperatures of lead and niobium [11]. The temperature calibration is confirmed by measurements on a variety of other paramagnetic substances. The magnetic field is determined by the currents in the coils of the superconducting magnet and was checked by the measured magnetic flux difference of the two manganese(II) salts at the superconducting transition temperature of lead and niobium, and proton NMR absorptions measured directly within the susceptometer. Each sample of $HgCo(NCS)_4$ was prepared by the literature method [2].

Several single crystals of the manganese Tutton salt, $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$, were ground to spheres weighing from 3.1 to 90 mg and were used as point dipole calibrants. A 52.4 mg sample of hexakis(pyridine N-oxide)maganese(II) perchlorate was used as a powder calibrant check. $HgCo(NCS)_4$, from several independent preparations, was measured as powder samples with sample weights in the 100–

200 mg range and as a 7 mg point dipole. All samples were packed into quartz tubes and the readings of the magnetization were corrected for both tube diamagnetism and the diamagnetism of the sample using Pascal's constants. Various magnetic fields ranging from 80 to 3800 gauss were used. Measurements in the range 5–300K were made on a Foner vibrating sample magnetometer [12], and these agreed well with the SQUID data, and also with the high temperature limit previously obtained [2], but not with either of the previous variable temperature studies [3, 4]. We are grateful to Prof. H. B. Gray for access to this instrument and to Dr A. Schweizer for assistance with the measurements.

Magnetic susceptibilities in the range 1.3–4.2K were recorded as before on a modified SQUID magnetometer, using a 94.6 mg sample of $HgCo(NCS)_4$. Magnetic field and temperature calibrations were made from NMR and helium vapor measurements, respectively.

TABLE I. Gram Susceptibility and Temperature Data for $HgCo(NCS)_4$ and the Two Manganese(II) Calibration Salts.

T	$CoHg(NCS)_4$	$Mn(PNO)_6(ClO_4)_2$	Mn Tutton
1.305	1785		
1.445	1675		
1.70	1509		
1.990	1379		
2.390	1232		
2.900	1093		
3.226	1025		
3.611	954		
3.911	904		
4.202	862		
4.50	838	1109	2500
5.21	758	964	2159
5.91	691	854	1901
6.91	613	733	1622
8.02	544	634	1397
9.23	484	553	1210
10.56	430	484	1057
11.92	386	430	935
13.15	353	390	847
14.20	329	362	784
15.64	300	329	711
16.50	285	312	674
17.26	273	299	644
18.06	262	286	615
18.89	251	273	588
19.62	241	263	566
20.27	235	255	548
20.91	227	247	531
21.56	220	240	515
22.21	214	232	501
22.83	209	226	486
23.66	202	218	469
24.72	193	209	449
25.77	185	201	430
27.87	170	185	398
31.43	153	164	354
37.58	128	138	295
45.64	105	113	243
53.76	89.8	96.4	206
61.66	78.0	84.8	177
68.88	69.7	75.5	160
75.72	62.8	68.7	145
82.85	57.9	62.9	132
91.00	53.5	58.1	122
96.85	49.9	53.6	113
102.60	46.4	50.3	107

Results and Discussion

The uncorrected χ_g data in the range 4–100K are given in Table I for a single 103.6 mg sample of $HgCo(NCS)_4$, as well as the two calibrant manganese salts at the same temperatures. Different runs on $HgCo(NCS)_4$ had maximum deviations in the absolute values of the moments of about 2%, but with much smaller standard deviations at given temperatures. The accuracy of relative values within a given run was much higher. Figure 1 shows the spread of the results together with the earlier low temperature literature data [4] for $HgCo(NCS)_4$. The validity of the literature synthesis of $HgCo(NCS)_4$ was established by analyses (Galbraith) which indicated Hg/Co rations of 1.00 ± 0.01, and different samples analyzed as well as duplicates on the same sample. The observed temperature dependence of the effective magnetic moment μ_{eff} is reproducible (a number of different samples used to check the results each reproduce this temperature dependence), real (the known susceptibilities of the two manganese(II) salts are accurately reproduced), and, because of the low field used, is unaffected by paramagnetic saturation: the biggest error is always the measurement of sample density (*e.g.* length of sample in sample tube, and mass of sample). There is no dependence on the particular sample preparation for several prepared by different people over several years.

The Gouy balance data (80–300K) of Figgis and Nyholm [3] have μ_{eff} decreasing markedly with falling temperature ($\theta = -10^\circ$ in $\chi \propto (T - \theta)^{-1}$) which would indicate a *strong antiferromagnetic* interaction. On the other hand, the Faraday balance data [4] (5.6–300K) has μ_{eff} increasing with decreasing temperature (θ = 2K) which indicates a fairly strong *ferromagnetic* interaction. In the overlap temperature region, the highly accurate SQUID susceptibilities lie well above the 80–300K Gouy data, but below the 5.6–300K data. At the lowest temperatures, our data disagree more markedly, both qualitatively and quantitatively with the Faraday data. The disagreement is presumably due to the existence, in the literature data, of errors in the temperature, the least accurate of all the parameters

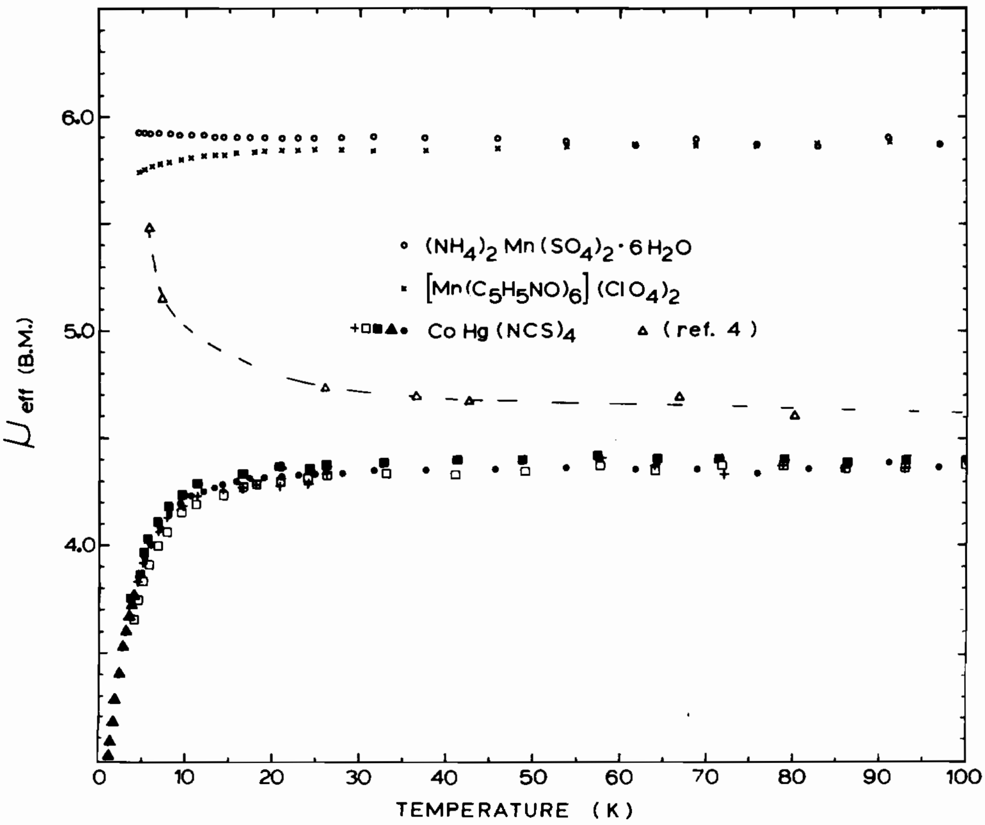

Figure 1. Temperature dependence (1.5–100K) of the effective magnetic moment (μ_{eff}). The dashed curve represents earlier literature data for $HgCo(NCS)_4$.

involved in the techniques [3, 4] used. Temperature errors appear to be the rule rather than the exception, and even physically impossible temperatures [12] can be indicated by temperature sensors calibrated by reference standard tabulated data. Since postulates of qualitatively different phenomena may be based on smaller deviations than the temperature errors (as in Figure 1), independent temperature calibration is strongly recommended.

The data reported by Hatfield *et al.* [7] using a vibrating sample magnetometer show agreement to within 2% of our reported data using a SQUID magnetometer. The SQUID method provides the most accurate and precise measurement of magnetic susceptibility. The agreement between the SQUID and vibrating sample magnetometer data further highlights the larger experimental error in the other two studies.

Figure 2 shows the temperature dependence, in the range 4–100K, of the inverse molecular susceptibility with the line representing the best least squares fit of the data to the Curie–Weiss law $\chi_M = c/(T - \theta)$. The resulting parameters give a Curie constant c = 2.41 cgs K^{-1} and $\theta = -0.62K$. Using a diamagnetic correction of 141.8×10^{-6} cgs/mol, the susceptibility can be accurately calculated from room

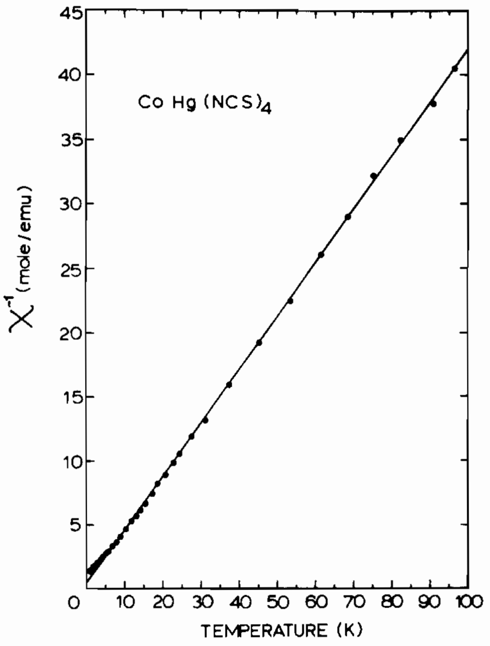

Figure 2. Plot of the temperature dependence of the inverse molecular susceptibility of $HgCo(NCS)_4$; the line shows the Curie–Weiss law fit of the data.

temperature down to about 20K. The calculated χ_g at 20 °C is 16.50×10^{-6} cgs/mol compared with the accepted value of 16.44×10^{-6} cgs/mol, excellent agreement considering an extrapolation of 200K. At lower temperatures, there is a marked deviation from Curie–Weiss behavior, presumably due to antiferromagnetic interactions *(vide infra)*, and caution must be used in using $HgCo(NCS)_4$ as a calibrant.

The magnitude of μ_{eff} for $HgCo(NCS)_4$ decreases rapidly at very low temperatures. Qualitatively, a weak antiferromagnetic interaction or zero-field splitting can cause such behavior. The cobalt(II) environment is tetrahedral [14], and, *in the absence of magnetic exchange,* the magnetic properties are described to sufficient accuracy by the Hamiltonian

$$H = D[S_z^2 - \frac{1}{3}S(S+1)] + g\beta \mathbf{H}\cdot\mathbf{S} \qquad (1)$$

where g = 2.26, from the Curie–Weiss fit, S = 3/2, and the other symbols have their usual meanings. Expressions reported by Figgis for the principal molecular magnetic susceptibilities are incorrect. However the correct equations may be derived from the Van Vleck equation [15].

The parallel and perpendicular zero field susceptibilities for S = 3/2 with an axial crystal field distortion are

$$\chi_{\parallel} = \frac{Ng^2\beta^2}{4kT} \cdot \frac{1 + 9e^{-x}}{1 + e^{-x}} \qquad (2a)$$

$$\chi_{\perp} = \frac{Ng^2\beta^2}{4kT} \cdot \frac{4 + \frac{6}{x}(1 - e^{-x})}{1 + e^{-x}} \qquad (2b)$$

where x = 2D/kT. The powder susceptibility $\chi_p = 1/3(\chi_{\parallel} + 2\chi_{\perp})$, assuming isotropic g-values, is then

$$\chi_p = \frac{Ng^2\beta^2}{kT} f(x) \qquad (3)$$

where

$$f(x) = \frac{3 + \frac{4}{x} + (3 - \frac{4}{x})e^{-x}}{4(1 + e^{-x})}$$

f(x) is an even function with respect to x and therefore powder measurements can only give the magnitude of D and will not resolve the sign.

The minimum value for the effective magnetic moment may now be calculated from eq. 3. As the temperature approaches zero, the limiting value of f(x) is 0.75. Since $\mu_{eff}^2 = 3g^2 f(x)$, the low temperature limit for μ_{eff} is 1.5g. The observed values fall well below this limit in the experimental temperature range, and the rate of decrease of μ_{eff} is greatest at the lowest temperature, indicating that the lower limit of μ_{eff} is well below any of the observed values. Clearly, zero field splitting cannot account for the observed magnetic properties and *antiferromagnetic exchange interactions* must therefore be present.

Further magnetic and analytical data are available [16].

Acknowledgement

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