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Low-temperature magnetic measurements of an $S=1$ linear-chain Heisenberg antiferromagnet

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The temperature-dependent magnetic susceptibility, $\chi(T)$, of two pure samples of the $S=1$ linear-chain Heisenberg antiferromagnet $Ni(C_2H_8N_2)_2NO_2(ClO_4)$, commonly known as NENP, has been measured from approximately 300 K to 300 μK. Our measurements of $\chi(T)$ are in agreement with existing results of other researchers who worked above 1.2 K. Below 1.2 K, $\chi(T)$ increases with decreasing temperature. The results suggest that the low-temperature increase of $\chi(T)$ is not a consequence of a single source of paramagnetic impurities in the samples but may arise from $S=\frac{1}{2}$ end-chain interactions.

Low-dimensional magnetic systems have been studied extensively since the birth of quantum mechanics.[1-3] This field of study received a surprise in 1983 when Haldane suggested[4] that a one-dimensional Heisenberg antiferromagnet (1D HAF) with integer spin possessed an energy gap between the nonmagnetic ground state and the first excited one. Furthermore, this Haldane gap was not present in noninteger spin systems. Haldane's report motivated a substantial body of theoretical[5,6] and experimental[7,8] work. The theoretical work extended the study to systems that more closely mimicked the real world by incorporating magnetic anisotropy and three-dimensional effects. This latter work indicates that, with sufficiently small magnetic anisotropy and with the intrachain magnetic (or exchange) interactions, J, stronger than the interchain ones, J', the quantum disordered ground state should persist to $T=0$.[9-13]

To date, experimental work suggests that a number of $S=1$, 1D HAF systems possess a Haldane gap, with $CsNiCl_3$ (Ref. 7) and $Ni(C_2H_8N_2)NO_2(ClO_4)$, commonly known as NENP,[8,14] receiving the most attention. Whereas $CsNiCl_3$, with $J'/J\simeq 1.2\times 10^{-2}$, possesses a three-dimensional long-range ordering (3D LRO) below $T_N\simeq 4.5$ K,[7] NENP, with $J'/J\simeq 4\times 10^{-4}$,[15] shows no sign of 3D LRO down to 1.2 K.[14-26] In fact, for NENP, the 1D quantum fluctuations along the chain ($J\simeq 48$ K) are sufficiently strong compared to the 3D interactions ($J'\simeq 20$ mK), the Haldane gap ($E_g\simeq 13$ K), and the single-ion anisotropy effects ($D\simeq 10$ K) that the system might remain unordered to $T=0$.[9-13]

We have measured the temperature-dependent magnetic susceptibility, $\chi(T)$, of two pure samples of NENP from room temperature to below 10 mK. Sample No. 1 was studied from 300 K to 264 μK, while sample No. 2 was investigated from 400 K to 6 mK. There are several existing measurements of $\chi(T)$ for $T>1.2$ K,[14-16,18-20] and our results are in agreement with these reports. Below 1.2 K, $\chi(T)$ increases with decreasing temperature. The results suggest that the low-temperature increase of χ is not a consequence of a single source of paramagnetic impurities in the samples or the measuring apparatus. Although the specific origin of the large susceptibility at low temperatures is difficult to identify from our results, the observed increase may arise from $S=\frac{1}{2}$ end-chain interactions.[16,27,28]

Two pure[29] NENP samples were grown according to the procedures outlined by Meyer *et al.*[14] Sample No. 1 was an orthorhombic single crystal, nominally $0.22\times 0.21\times 0.81$ cm^3, with the b axis (Ni-chain axis) along the longest direction, and had a mass of approximately 44.15 mg. Sample No. 2 was a quasiorthorhombic-shaped crystal nominally $0.23\times 0.22\times 0.76$ cm^3, slightly polycrystalline in the a-c plane with the b axis aligned along the longest direction, and had a mass of approximately 47.66 mg.

Magnetization measurements were made from 1.8 to 400 K in magnetic fields ranging from 10 mT to 0.5 T, $\hat{\mathbf{B}}\|\hat{\mathbf{b}}$. A small background contribution arising from the sample holder has been measured and subtracted from the data, Fig. 1. The magnetometer[30] is able to measure absolute values of $\chi(T)$. Systematic error in these values arises from uncertainties associated with the calibration of the magnetic field and the small background signal. These errors are estimated to be $\pm 5\%$ for the magnetic field and approximately ± 1.0 memu/mol for the background. The error bars shown in Figs. 1 and 2 reflect

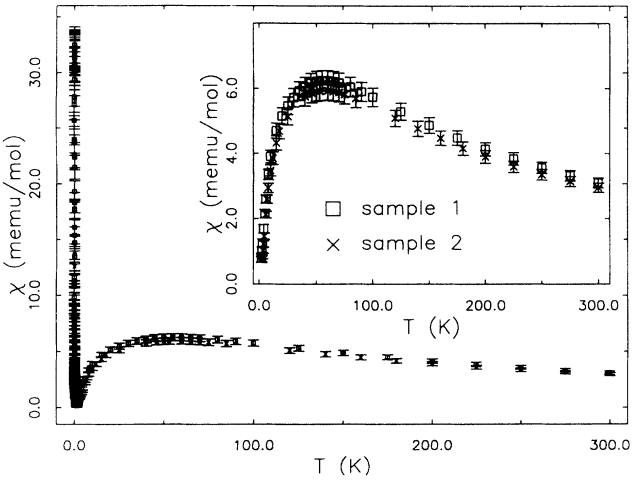

FIG. 1. The $\chi(T)$ data for both samples is shown. The inset shows the high-temperature results obtained from the magnetometer measurements. The error bars reflect systematic uncertainties as explained in the text.

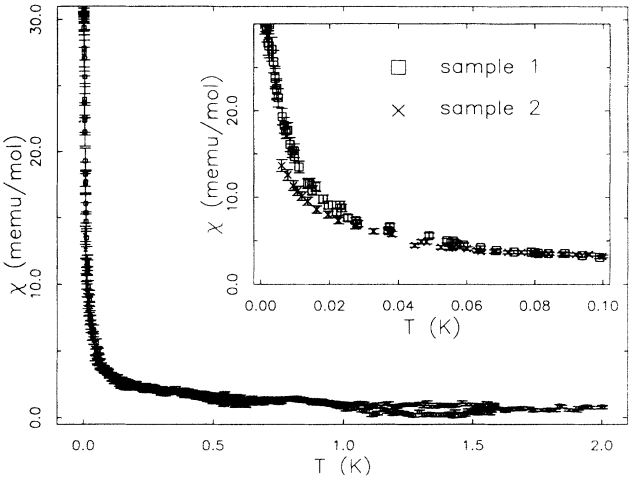

FIG. 2. The $\chi(T \leq 2.0K) \leq 30$ memu/mol data for both samples is shown. The inset shows $\chi(T \leq 0.1K) \leq 30$ memu/mol. Below 80 mK, $\chi(T)$ for the two samples becomes noticeably different. The error bars reflect systematic uncertainties as explained in the text.

these limits. As described below, the uncertainties are maintained while normalizing the low-temperature data to obtain absolute $\chi(T)$ values.

Low-temperature low-frequency susceptibility studies were performed from 40 mK to 2.0 K using standard mutual inductance techniques operating at 317 Hz, $B_{ac} < 10$ μT_{rms} and $\hat{\mathbf{B}}_{ac} \| \hat{\mathbf{b}}$, in the earth's magnetic field. The measured $\chi(T)$ was independent of frequency from 3.17 to 317 Hz at $T = 48$ and 121 mK. The contribution to $\chi(T)$ arising from the coil and thermalizing Cu wires, which were varnished[31] to the specimens, was measured after the samples were removed. This temperature-dependent background has been subtracted from the data. Absolute $\chi(T)$ values were obtained by normalizing the data to the results of the magnetometer measurements in the overlapping temperature region, Figs. 1 and 2.

In a third apparatus, our investigations were performed from approximately 150 mK down to below 10 mK. Susceptibility measurements were performed with an ac mutual inductance bridge, operating at 16 Hz with $B_{ac} \sim 0.2$ μT_{rms} and $\hat{\mathbf{B}}_{ac} \| \hat{\mathbf{b}}$, using a rf superconducting quantum interference device (SQUID) as a null detector. Measurements on sample No. 1 were performed using a detection coil arrangement described elsewhere.[32] Four 0.76-mm-diam Ag wires[33] were Ag epoxied[34] into a Cu base that was bolted to the top of a Cu nuclear demagnetization stage. The sample was Ag painted[35] into the region of the first pick-up coil with the Ag wires extending through the second, counterwound pick-up coil. An equal amount of Ag paint was placed in the region of the second coil. Although the background from the Ag wires and paint was not measured directly and, hence, was not subtracted from the data, Figs. 1 and 2, these contributions, in principle, were compensated by the astatic pick-up coil arrangement. For measurements up to 165 mK, the temperature of the detection coil–shield assembly was kept constant, as the temperature of the sample (plus Ag wires and paint) was changed. Consequently, any potential temperature dependence of the background susceptibility arising from the detection assembly did not affect the results. Absolute susceptibility values were obtained by normalizing the data to the aforementioned millikelvin results. An independent check of the relative $\chi(T)$ values is also possible, since a knowledge of the sample-coil geometry permits measured mutual inductance differences to be converted to relative susceptibility shifts $\Delta\chi(T)$. Prior to normalizing the data to define the absolute values, this method of obtaining $\Delta\chi(T)$ agreed with the ones obtained from the millikelvin experiment in the overlapping temperature region.

An interesting observation was made above and below ~ 4 mK.[36] Above 4 mK, the response of the sample to a temperature change was rapid, with a characteristic time constant less than 3 min. Below 4 mK, a distinctive thermal relaxation appeared, with a time constant estimated to be greater than 20 min. Such an abrupt increase in the thermal relaxation of the sample is often an indication of an increase in the specific heat of the specimen. In addition, $\chi(T)$ appeared to be essentially temperature independent from 1 mK down to 264 μK. Although a temperature-independent signal is indicative of a decoupling between the thermometer and sample, it may also reflect an ordering in the specimen.

For sample No. 2, another pick-up coil assembly, which was essentially of the same design as the previous one, was used. To avoid any possible magnetic signal arising from Fe impurities in the Ag paint,[35,37] the sample was varnished[31] to the thermally anchoring Ag wires.[33] With these conditions, sample No. 2 was investigated down to 6 mK. The relative or absolute $\chi(T)$ values were checked or established in the same manner described for sample No. 1.

As mentioned earlier, our susceptibility results above 1.2 K, Figs. 1 and 2, are in agreement with the ones reported by previous workers.[14–16,18–20] Following Meyer *et al.*,[14] an analytical expression for $\chi(T)$ of a 1D HAF

TABLE I. As described in the text, fits to the data over the temperature ranges indicated have provided the values tabulated. The fits were weighted by experimental uncertainties, Fig. 1 and 2, as discussed in the text. The limits shown for each parameter are the 1σ statistical errors derived from the nonlinear least-square fits. The parameters are defined in the text.

Sample number	J (K) ($T \geq 20$ K)	g	E_g (K) (1.7 K $\leq T \leq$ 5.0 K)	C (10^{-4} emu K/mol) (6 mK $\leq T \leq$ 1.7 K)	Θ (mK)
1	46.2±0.6	2.11±0.01	12.4±3.9	2.20±0.04	−5.8±0.2
2	47.3±0.4	2.08±0.01	10.3±3.2	2.21±0.04	−11.9±0.4

with $S=1$, calculated by high-temperature expansion,[38] has been used for $T \geq 20$ K to obtain the values of J and g, the Landé factor, listed in Table I. The fits used to determine the parameters listed in Table I were weighted by the experimental uncertainties, which reflect estimates of systematic errors already discussed. The uncertainties listed in Table I are the 1σ statistical errors derived from nonlinear least-square fits. As suggested by Renard *et al.*,[15] we have used the expression $\chi(T) = \chi(0) + \beta \exp\{-E_g/kT\}$, from 1.7 to 5 K, to provide a rough estimate of the Haldane gap E_g, Table I. To fit over this range, data from both the millikelvin and high-temperature studies were used simultaneously. The results given in Table I are in excellent agreement with the values obtained by other workers using a variety of techniques.[8]

The striking aspect of our data is the large susceptibility increase at the lowest temperatures. One possible source of such a large increase in $\chi(T)$ at the lowest temperatures is the presence of paramagnetic impurities.[16] Therefore, we have fitted our data from 6 mK to 1.7 K with the standard expression $\chi(T) = \chi(0) + C/(T-\Theta)$, and the results are given in Table I. A significant result is that the Curie constants C and Weiss temperatures Θ are approximately equal for the two samples. Careful analysis of the NENP crystals[29] shows that paramagnetic impurities do not exist in sufficient numbers to explain the observed increase of $\chi(T)$ at low temperature.[37] It is important to recall that the low-temperature susceptibility increase was observed in several dramatically different mounting arrangements, where background effects were either nullified, subtracted, or minimized through the use of pure construction materials. The most likely cause of the increase is end-chain effects. In any real material, the magnetic chains will be broken by the presence of impurities or structural defects. For broken chains, each end acts as an $S=\frac{1}{2}$, $g=2$ spin.[27,28] If our data is interpreted as arising from independent $S=\frac{1}{2}$ spins, then a Curie constant of 2.2×10^{-4} emu K/mol would require an impurity concentration of approximately 500 ppm. If strictly associated with end-chain spins,[39] then 500 ppm would imply, on the average, the presence of NENP chains that are about 4000 Ni units long. Given the difficulty associated with growing crystals of this type of material,[14] we consider this number to be quite reasonable. Further insight may be gained through an analysis of Θ, which is a rough measure of the strength of the interactions between the spins responsible for the low-temperature susceptibility increase. Although Θ is antiferromagnetic for both specimens, its absolute value is somewhat larger for sample No. 2 when compared to sample No. 1 (see Table I). This result would be expected if end-chain spins were responsible for the results, since sample No. 2 is less uniform than sample No. 1. In addition, the abrupt appearance of a thermal relaxation in sample No. 1 below 4 mK is close to its $|\Theta| = 5.8\pm0.2$ mK. Although further experimental work is needed to clarify the issue, the behavior of dilute, isolated $S=\frac{1}{2}$ entities embedded in a sea of quantum disordered 1D, $S=1$ spins merits further theoretical attention.

On the other hand, there are other possible explanations which we cannot completely exclude. Firstly, the Ni outside the linear chains (i.e., in the form of either excess surface residue, isolated $S=1$, $g \simeq 2$ spins or Ni^{2+} ions) might generate an increase in the low-temperature $\chi(T)$, and approximately 200 ppm of these spins would be required to explain our observations.[39] If the defects in the chains are randomly distributed with concentration x, there will be single isolated Ni^{2+} ions with probability per site proportional to x^2, but this effect, as constrained by the size of the Curie constant, should be too small to explain our results. Finally, the Curie constant might also be interpreted in terms of the linear-chain Ni spins participating in some type of 3D LRO; however, an established microscopic model is needed before we can consider this mechanism further.

In conclusion, we have observed a strong increase in the magnetic susceptibility of NENP below 150 mK. The most likely explanation of the susceptibility increase is related to $S=\frac{1}{2}$ end-chain interactions; however we cannot completely exclude the possibility that our observations are a consequence of the summation of several small contributions. Our results indicate that new crystal growth methods are necessary before making further progress on the issue of NENP remaining disordered as $T \to 0$.

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[1]H. A. Bethe, Z. Phys. **71**, 205 (1931).

[2]L. J. de Jongh and A. R. Miedema, Adv. Phys. **23**, 1 (1974), and references therein.

[3]M. Steiner, J. Villain, and C. G. Windsor, Adv. Phys. **25**, 87 (1976),and references therein.

[4]F. D. M. Haldane, Phys. Lett. **93A**, 464 (1983); Phys. Rev. Lett. **50**, 1153 (1983).

[5]J. C. Bonner, J. Appl. Phys. **61**, 3941 (1987), and references therein.

[6]I. Affleck, J. Phys. Condens. Matter **1**, 3047 (1989), and references therein.

[7]M. Steiner, J. Appl. Phys. **67**, 5593 (1990), and references therein.

[8]J. P. Renard, V. Gadet, L. P. Regnault, and M. Verdaguer, J. Magn. Magn. Mater. **90&91**, 213 (1990), and references therein.

[9]Yu. A. Kosevich and A. V. Chubukov, Zh. Eksp. Teor. Fiz. **91**, 1105 (1986) [Sov. Phys. JETP **69**, 654 (1987)].

[10]I. Affeck, Phys. Rev. Lett. **62**, 474 (1989).

[11]H. Tasaki, Phys. Rev. Lett. **64**, 2066 (1990); **66**, 798 (1991).

[12]T. Sakai and M. Takahashi, Phys. Rev. B **42**, 4537 (1990).

[13]E. F. Shender and S. A. Kivelson, Phys. Rev. Lett. **66**, 2384 (1991).

[14]A. Meyer, A. Gleizes, J. J. Girerd, M. Verdaguer, and O. Kahn, Inorg. Chem. **21**, 1729 (1982).

[15]J. P. Renard *et al.*, Europhys. Lett. **3**, 945 (1987).

[16]J. P. Renard, L. P. Regnault, and M. Verdaguer, J. Phys. (Paris), Colloq. **49**, Suppl. 12, C8-1425 (1988).

[17]J. Ferre, J. P. Jamet, C. P. Landee, K. A. Reza, and J. P. Renard, J. Phys. (Paris), Colloq. **49**, Suppl. 12, C8-1441 (1988).

[18]K. Katsumata *et al.*, Phys. Rev. Lett. **63**, 86 (1989).

[19]K. Katsumata *et al.*, Prog. Theor. Phys. Suppl. **101**, 503 (1990). These authors report that the high magnetic-field magnetization does not change from 1.3 to 0.51 K.

[20]Y. Ajiro, T. Goto, H. Kikuchi, T. Sakakibara, and T. Inami, Phys. Rev. Lett. **63**, 1424 (1989).

[21]T. Goto, N. Fujiwara, T. Kohmoto, and S. Maegawa, J. Phys. Soc. Jpn. **59**, 1135 (1990).

[22]P. Gaveau, J. P. Boucher, L. P. Regnault, and J. P. Renard, Europhys. Lett. **12**, 647 (1990).

[23]M. Date and K. Kindo, Phys. Rev. Lett. **65**, 1659 (1990).

[24]P. Gaveau, J. P. Boucher, L. P. Regnault, T. Goto, and J. P. Renard, J. Appl. Phys. **69**, 5956 (1991).

[25]M. Chiba, Y. Ajiro, H. Kikuchi, T. Kubo, and T. Morimoto, Phys. Rev. B **44**, 2838 (1991); **45**, 5119 (1992); J. Magn. Magn. Mater. **90&91**, 221 (1990).

[26]W. Lu, J. Tuchendler, M. von Ortenberg, and J. P. Renard, Phys. Rev. Lett. **67**, 3716 (1991).

[27]M. Hagiwara, K. Katsumata, I. Affleck, B. I. Halperin, and J. P. Renard, Phys. Rev. Lett. **65**, 3181 (1990).

[28]S. H. Glarum, S. Geschwind, K. M. Lee, M. L. Kaplan, and J. Michel, Phys. Rev. Lett. **67**, 1614 (1991).

[29]The materials used to make the crystals contained impurity levels of (all in ppm) Ca=10, Co=40, Mg=10, and Na=10. Inductively coupled Ar plasma atomic emission spectrometry of the resultant crystals indicated impurity levels of B=20, Mg=0.2, Si=50, S=10, Ca=2, Na=500, Mn<0.2, Fe<1, Co<1, Cu<2 and others <10. The Na residue arises from the use of $NaNO_2$ in the fabrication process, with some Na ions remaining on the surface of the crystals.

[30]Quantum Design Inc., San Diego, CA 92121.

[31]Varnish 7031 made by General Electric and sold by local distributors.

[32]O. Avenel *et al.*, Phys. Rev. B **45**, 5695 (1992).

[33]Materials Research Corporation, Orangeburg, NY 10962. Martz grade with typical results of emission spectroscopy (all in ppm): Al=3, Bi<3, Cu<2, Fe<3, Mg<2, Ni<2, Pb<3, Si<3, Sn<2, V<1.

[34]H31LV, Epoxy Technology Inc., Billerica, MA 01821.

[35]Johnson Matthey, Materials Technology, Royston, Herts, UK. Catalog Number P3100, the Ag component (54% by weight), contains (all units ppm) Fe up to 1000, typically 200–800, Ni typically <500, and others <100. No impurity information is available on the organic components.

[36]O. Avenel *et al.*, J. Low Temp. Phys. (to be published).

[37]For example, consider the case of Fe, which may exist in either the 2+ or 3+ states. Approximately 50 ppm of this type of impurity is necessary to explain the Curie constants, Table I.

[38]C. Y. Weng, Ph.D. thesis, Carnegie Institute of Technology, 1968 (unpublished).

[39]In an attempt to measure paramagnetic impurities and/or end-chains spins, EPR was performed at 9.55 GHz, $\hat{\mathbf{B}} \perp \hat{\mathbf{b}}$. A 10-mg sliver of sample No. 1 was studied at room temperature, 4.2, 2.1, and 1.8 K. [See Refs. 27 and 28 and P. P. Mitra, B. I. Halperin, and I. Affleck, Phys. Rev. B **45**, 5299 (1992).] No resonances were observable above the noise at any temperature from 0.25 to 0.4 T, with a sensitivity of $\sim 10^{19}$ spins for a 500-G linewidth.