Observation of Fractional Spin $S=\frac{1}{2}$ on Open Ends of $S=1$ Linear Antiferromagnetic Chains: Nonmagnetic Doping

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Approximately 0.5% of nonmagnetic divalent ions Zn, Cd, and Hg have been alternately substituted for Ni in the linear chain of antiferromagnetically coupled Ni^{2+} ($S=1$) spins in $[Ni(C_2H_8N_2)_2(NO_2)]ClO_4$ (NENP). While at low temperature the pure NENP shows no EPR signal, the doped NENP shows identical EPR spectra corresponding to the fractional spin $S=\frac{1}{2}$ states at the "open" ends of the Ni chains adjacent to the nonmagnetic substitutions.

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A great deal of interest in one-dimensional chains with nearest-neighbor antiferromagnetic (AF) Heisenberg exchange coupling, J, has been stimulated by Haldane's [1] observation that closed integer spin chains have a finite gap, Δ_H, in the excitation spectrum above a singlet ground state, in contrast to half-integer spins which would be gapless with a continuum of excited states above the ground state. $[Ni(C_2H_8N_2)_2(NO_2)]ClO_4$ (NENP) has an orthorhombic crystal structure with the Ni^{2+} ($S=1$) ions arrayed in linear chains along the b axis and AF coupled by superexchange, through bridging NO_2 ions [2]. The interchain coupling is many orders of magnitude weaker making NENP an ideal one-dimensional AF chain. While the Ni is sixfold coordinated in a near octahedron by five N and one O ligands, the true site symmetry is lower than cubic and the appropriate Hamiltonian would be

$$\mathcal{H}=\sum_i [J_x S_i^x S_{i+1}^x + J_y S_i^y S_{i+1}^y + J_z S_i^z S_{i+1}^z + D S_{iz}^2 + E(S_{xi}^2 - S_{yi}^2)]\,, \qquad (1)$$

where z is along the chain axis. Recent estimates [3] based upon a fit to the observed high-temperature susceptibility indicate an average $J \sim 44$ K and $D \sim 9\ \mathrm{K} \gg E$. Neither D nor the exchange anisotropy are large enough to destroy the singlet ground state and Haldane gap [4]. Magnetization measurements have verified the singlet ground state [5,6], EPR studies have revealed the triplet excited state [7], and excitations at the gap have been studied by neutron scattering [6].

The valence bond solid model [8] applied to the one-dimensional Heisenberg chain of $S=1$ spins with nearest-neighbor AF coupling provides a good description and intuitive picture of the ground state. In this model the spin 1 on each site is represented by symmetrization of two spin $S=\frac{1}{2}$ variables. For a *closed* chain, the many-body $S=0$ ground state is then formed by two valence bonds originating from each site to form singlets with adjacent neighbors. For an *open* chain, however, unpaired bonds are left at each end of the chain which remarkably correspond to effective fractional spins $S=\frac{1}{2}$ at the ends of the chain. This is borne out as well by exact diagonalization [9] of finite open chains which show the four lowest-lying states to be a triplet and singlet whose energy separation approaches zero exponentially with increasing chain length with the next excited state at the Haldane gap. This approach to zero separation corresponds to vanishing interaction between the effective spins of $\frac{1}{2}$ at the ends of the chain. Recently Cu^{2+} has been diluted into NENP, the Cu^{2+} serving to break the Ni^{2+} chains [10]. The EPR spectrum observed was interpreted in terms of the $S=\frac{1}{2}$ of the Cu^{2+} AF coupled to the $S=\frac{1}{2}$ spins at the ends of the Ni^{2+} chain adjacent to the Cu^{2+}. An indication of the difficulty in understanding the full spectrum was the use of a Hamiltonian with axial symmetry around the b axis in spite of the fact that considerable anisotropy was seen as H_0 was rotated in the a-c plane.

In order to provide a simpler break in the chain we have substituted approximately 0.5% of the nonmagnetic ions Zn, Cd, and Hg for the Ni. The crystal lattice constants were measured and were indistinguishable from pure NENP [11]. No EPR resonances were observed at low temperature in undoped NENP. When doped with approximately 0.5% Zn, a *single* resonance line with $g_b=2.140$ is observed with $H_0 \| b$ as shown in Fig. 1, curve a. The line is Lorentzian and approximately 110 G wide. $d\chi''/dH$ was recorded with 3-G, 100-kHz modulation and lock-in detection. This resonance is ascribed to the free spins $S=\frac{1}{2}$ at the ends of the chains adjacent to the Zn substitution as will be further detailed below. No interaction between these $S=\frac{1}{2}$ spins on opposite sides of the Zn is seen and if present is within the observed linewidth. This line splits in two with $H_0 \| a$ (Fig. 1, curve b). Each of these lines splits further as H_0 is rotated in the a-c plane as shown in Fig. 1, curve d, for H_0 at 45° to the a axis in the a-c plane. Two lines are seen again with $H_0 \| c$ (Fig. 1, curve c) but at different field values than for $H_0 \| a$.

On chemical grounds alone, the metal ions are expected to enter the lattice substitutionally for the Ni. In addition, we emphasize that the positions of the resonance lines for any given direction of H_0 in all the spectra are identical for three different nonmagnetic substitutions

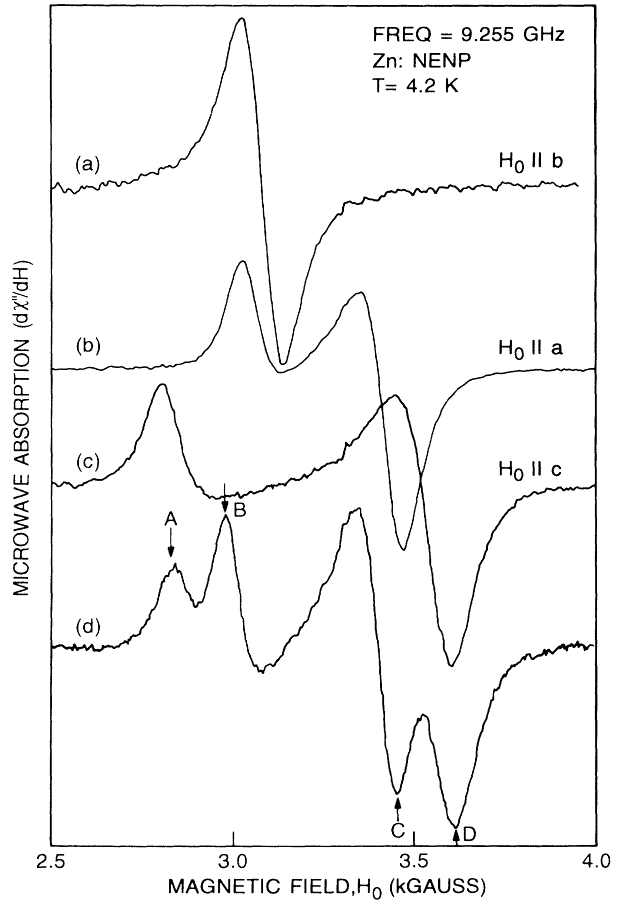

FIG. 1. EPR signal ($d\chi''/dH$) with 3-G ac modulation in ~0.5% Zn NENP (see text).

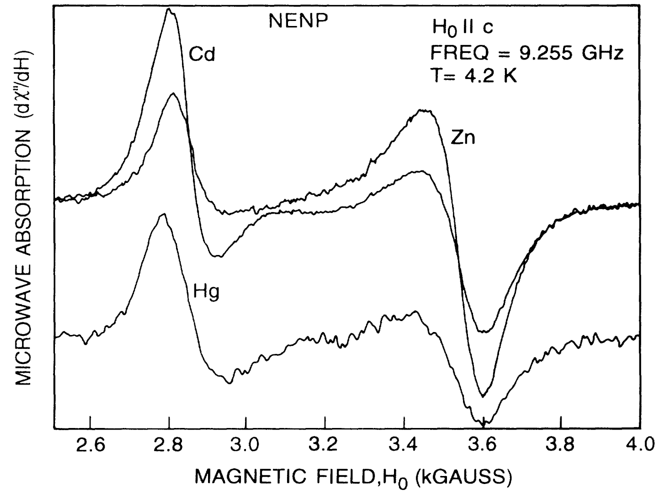

FIG. 2. EPR signal for ~0.5% Zn-, Cd-, and Hg-doped NENP. Similar spectra verify that the signal is from Ni chain ends adjacent to the impurity and not from a nonmagnetic dopant.

that have been made, i.e., Zn, Cd, and Hg, as illustrated, for example, in Fig. 2 for $H_0 \| c$. This clearly indicates that the nonmagnetic ions serve only to sever the chains and the observed EPR spectra are associated with the Ni near the chain ends. The only differences are in the relative amplitudes of different portions of the spectrum. For example, while the amplitude of the high-field line in Fig. 2 is somewhat greater than the low-field line, the situation is reversed for Cd and Hg and will be discussed further below. Note that except for $H_0 \| b$ the lines are not symmetric around $d\chi''/dH = 0$ and the integrated spectrum χ'' vs H for $H \| c$ corresponding to $d\chi''/dH$ in Fig. 1, curve *c*, is shown in Fig. 3. Thus what superficially appears as two lines in $d\chi''/dH$ in Fig. 1, curves *b* and *c*, really correspond to the extrema of a distribution. This distribution which will be discussed further below appears even more dramatically when the EPR spectrum is examined at 22.84 GHz as shown in the inset of Fig. 3.

The integrated intensity I of the EPR signal decreases with increasing temperature T much more rapidly than $1/T$ as illustrated for different temperatures in Fig. 3 and is similar to that observed for the Cu^{2+} substitution by Hagiwara, Katsumata, Affleck, and Halperin [10]. However, it is difficult to say anything precise about the Haldane gap Δ_H without better knowledge of the density of states at the gap, since a variety of empirical functions with Δ_H varying by a factor of 2 can fit the I vs T data.

To help clarify the origin of the splittings seen when H$_0$ is *not* along the chain axis, the spectra were studied at 22.84 as well as 9.25 GHz. It was found that all splittings and line positions, measured in gauss, *scale linearly with microwave frequency* from 9.25 to 22.84 GHz corre-

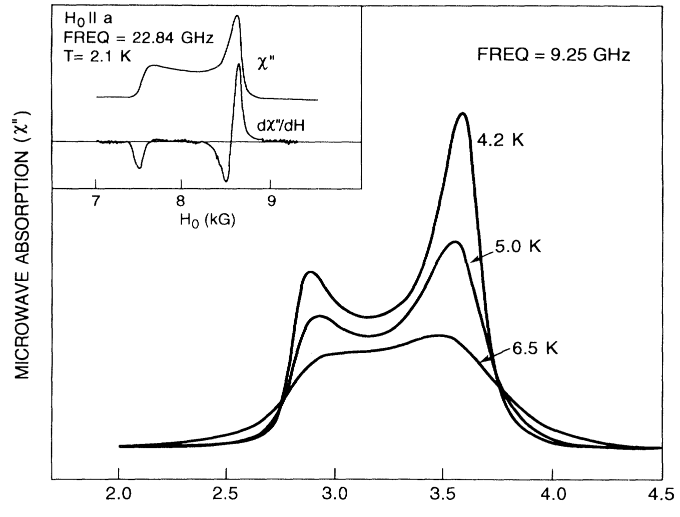

FIG. 3. Integration of $d\chi''/dH$ with $H_0 \| c$ from Fig. 1, curve *c*; also shown for two higher temperatures. Inset: $-d\chi''/dH$ and χ'' at 22.84 GHz, showing more dramatically the *distribution* in χ'' (see text).

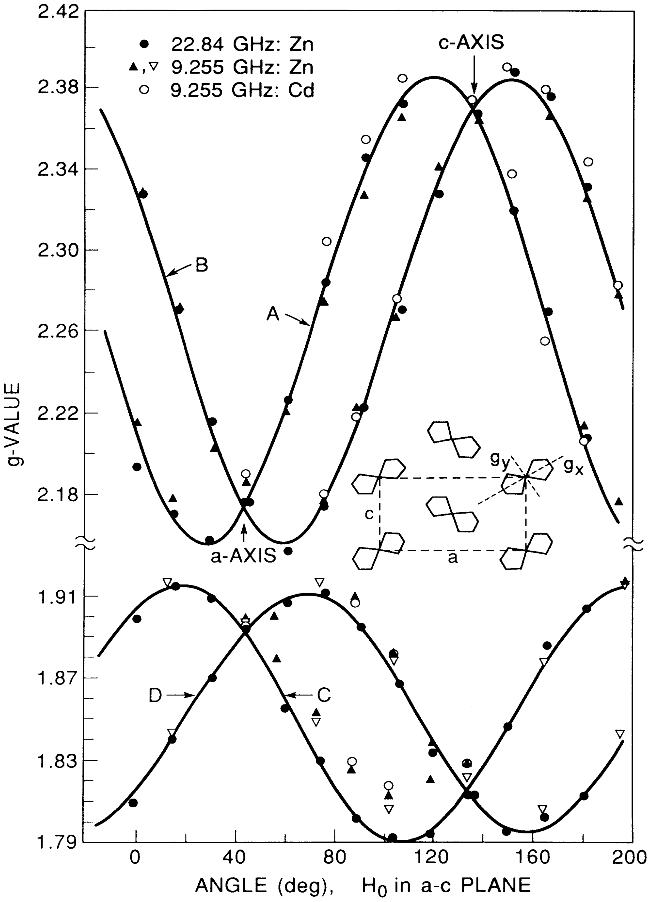

FIG. 4. Excursion of the peaks shown in Fig. 1, curve *d*, as H_0 is rotated in the *a-c* plane. The fact that splittings at different frequencies have the same *g* values verifies spin-$\frac{1}{2}$ behavior (see text).

sponding to a spin Hamiltonian

$$\mathcal{H} = \beta \mathbf{S} \cdot \overleftrightarrow{\mathbf{g}} \cdot \mathbf{H}_0 , \tag{2}$$

with $S=\frac{1}{2}$. The excursion of these spectra as H_0 is rotated in the *a-c* plane is plotted in Fig. 4 where the points shown correspond to those peaks in $d\chi''/dH$ marked by the arrows in Fig. 1, curve *d*. The solid lines are least-squares fits of the more accurate 22.84-GHz data by a functional form $g_\perp = g_x^2 \cos^2\theta + g_y^2 \sin^2\theta$. The departures of the 9.25-GHz data points from these lines could be due to crystal misorientation and large errors due to the poorer resolution of the splittings at this frequency.

If the splittings were due to interaction between the spins $\frac{1}{2}$ either adjacent to Zn or on the ends of the same chain, or to a spin value $S \geq 1$, terms of the type DS_z^2 would be added to $\mathcal{H}$ and to first order the splittings measured in gauss would be independent of microwave frequency contrary to what is observed. Since the density of the free spins $S=\frac{1}{2}$ decay exponentially over about 5-7 spins into the Ni chain, we tried to make chains short enough to see the interaction between the spins on the same chain by increasing the concentration of Zn. However, chemical analysis indicated that the maximum doping realized so far was always $< 1.2\%$ so that no such effects were seen.

The splittings of lines *A-B* and *C-D* are related to the two Ni chains in which the ethylene diamines are rotated around the *b* axis in opposite directions from the *a* axis as shown in Fig. 4. The expected local principal axes of the *g* tensor are labeled g_x, g_y in Fig. 4, with g_z along *b*. X-ray data [2] give 31.4° for the angle between the g_x and *a* axes, close to the value found for the *C,D* lines in Fig. 4, however, quite different from the angle of 14° for lines *A-B*. One interpretation of these results is that *A,B* and *C,D* correspond, respectively, to different environments. For example, some of the Zn (*C,D*) may substitute for the Ni without changing the local environment in any way while some *A,B* may distort the surroundings to conform to the pure Zn compound $[\mathrm{Zn(en)_2(NO_2)}]\mathrm{ClO_4}$ which is triclinic. The *g* values at these two extrema are $g_x^{A,B}=2.386$, $g_y^{A,B}=2.157$, $g_x^{C,D}=1.915$, $g_y^{C,D}=1.790$ with $g_z(H_0 \| b)=2.140$ in all cases. Perhaps a range of sites exist between the two extrema *A,B* and *C,D* (which are preponderant) corresponding to different twists of the ethylene diamine which gives rise to the distribution in Fig. 3. The fact that the intensity of *A,B* relative to *C,D* is reversed for Zn relative to Cd and Hg suggests support for this conjecture as the Cd and Hg ions are considerably larger than Zn and might have a greater preference for the *A,B* sites compared to *C,D*. However, one is left with the puzzle of a *g* value of less than 2 for the *C,D* sites, whereas all known Ni^{2+} *g* values in octahedral coordination are greater than 2. In addition, while there is a significant spread in g_x and g_y, these supposed different sites have the same value of g_z.

This would suggest consideration of alternative explanations involving the incompletely understood behavior of the decay of the spin-$\frac{1}{2}$ distribution into the chain, and, in particular, the role played by the large positive DS_z^2 term, the smaller *E* term, and the exchange anisotropy in Eq. (1). It may be unlikely that any of these terms are large enough to create any further states below the gap other than the spin-$\frac{1}{2}$ states at each chain end. However, these terms along with their variation due to site inhomogeneity may influence the *g* values and their observed distribution. Further analytical work and computer simulations should address these problems [12]. Perhaps by actually measuring the decay of the spin-$\frac{1}{2}$ density into the chain by measuring the hyperfine fields in an enriched ^{61}Ni sample one will be able to answer some of these equations and gain a clearer understanding of these intriguing results.

In conclusion, we have shown that substitution of quite different nonmagnetic ions for the Ni^{2+} breaks the Ni chain and creates effective fractional $S=\frac{1}{2}$ states at the ends of the chains whose *g* values are independent of the type of nonmagnetic dopant.

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