

Dipolar Magnetic Order with Large Quantum Spin Fluctuations in a Diamond Lattice

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We report the first observation of dipolar magnetic order in a diamond lattice, in the $RPO_4(MoO_3)_{12} \cdot 30H_2O$ compounds ($R = Gd, Dy, Er$). Theory predicts antiferromagnetic order for a diamond lattice of dipoles, with a susceptibility at $T=0$ depending only on lattice symmetry and spin. We present experimental susceptibilities for ions with different effective spin which are consistent with these predictions, and which confirm the existence of unusually large quantum spin fluctuations in these materials. The fluctuations substantially exceed those of the Heisenberg antiferromagnet.

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Dipolar magnetic order is an interesting problem because the dipolar Hamiltonian is known exactly, presenting the opportunity for a critical comparison between theory and experiment. Cubic lattices occupy a position of special importance, due to their simplicity and, more importantly, the fact that ion moments are isotropic, resulting in magnetic order that is determined by lattice symmetry alone. Isotropy should also produce the largest spin fluctuations. Among the primitive cubic lattices, bcc and fcc are predicted always to be dipolar ferromagnets, while only simple cubic is predicted to be antiferromagnetic [1,2]. The antiferromagnetic case is of particular interest because it is here that quantum fluctuations are most directly observable, as we discuss below. The most accessible model systems for studying the full dipolar Hamiltonian are dilute rare earth insulating compounds. While several such materials exist with fcc symmetry [3], it is unfortunate from the experimental standpoint that no simple cubic examples are known.

There does exist, however, at least one excellent model system with diamond structure, which we find is also predicted to exhibit dipolar antiferromagnetism. This is the rare earth (R) phosphomolybdate tridecahydrate series, $RPO_4(MoO_3)_{12} \cdot 30H_2O$. We have carried out magnetic measurements on the Gd, Dy, and Er members of this series which are consistent only with antiferromagnetic order [4]. They also confirm the existence of unique and very large spin wave zero-point motion effects, directly observable in the susceptibility.

The classical ground state energy per spin of a cubic lattice of point dipoles is

$$E_0 = -\frac{1}{2} \lambda n (g \mu_B S)^2, \quad (1)$$

where λ is a dimensionless, maximal eigenvalue of the dipolar field matrix, and n is the spin density. For diamond, we find $\lambda_{dia} = 6.394$ [5]. The predicted spin configuration is a layered structure, with four sublattices aligned in pairs along the cubic (110) axes. It is pictured in Fig. 1, using a tetragonal unit cell containing four spins, one from each sublattice. The magnitude of λ_{dia} exceeds that for the sc lattice, $\lambda_{sc} = 5.352$, and also that for ferromagnetic order (assuming the ferromagnet is

free to minimize its energy by splitting into domains), $\lambda_{FM} = 4\pi/3$. This establishes diamond as the most strongly antiferromagnetic and most stable of the cubic dipolar lattices. This result agrees with the observation that dipolar antiferromagnetism is favored by relatively open structures, in which a spin is surrounded by a small number of nearest neighbors with anisotropic angular distribution [6]. The minimum antiferromagnetic ground state energy in the cubic lattices has a monotonic behavior when plotted as a function of coordination number, as shown in Fig. 1.

The ordered diamond ground state is highly (sixfold) degenerate, so that one expects the experimental susceptibility to be isotropic and always equal to χ_{\perp} . Classically, this is temperature independent, given (per unit volume) by [1,7]

$$\chi_{\perp}^0 = (\lambda = 4\pi/3)^{-1}. \quad (2)$$

A mean field calculation yields the same value. This result is unique in that it depends only on lattice symmetry, through the eigenvalue λ . Unlike the corresponding re-

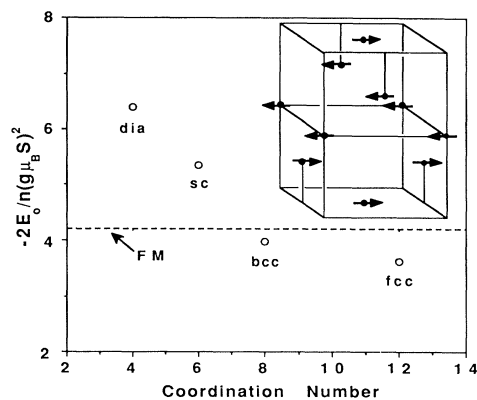


FIG. 1. The classical energy per spin of the lowest-lying antiferromagnetic arrays in cubic lattices, from Eq. (1), plotted as a function of coordination number. The dotted line is the corresponding ferromagnetic energy. Antiferromagnetism is predicted for sc and diamond. The inset shows the predicted four-sublattice Néel state for diamond, using a tetragonal unit cell.

sult for exchange-coupled antiferromagnets, it does not depend on interaction strength.

The $RPO_4(MoO_3)_{12} \cdot 30H_2O$ materials and related heteropoly acid salts are unique among ionic compounds in having perfect diamond structure, space group O_h^7 [8]. It forms in this structure apparently because of the tetrahedral shape of the $PO_4(MoO_3)_{12}^{3-}$ anion rather than any directionality of the bonds. Rare earths and phosphomolybdate ions form interpenetrating diamond lattices. The rare earth ions occupy sites of T_d symmetry. The cubic unit cell edge is 23.1 Å, with a nearest-neighbor separation between magnetic ions of 10.0 Å, so that the exchange interaction should be very small. This is confirmed by paramagnetic susceptibilities of spherical samples well above the magnetic ordering temperatures, which yield Weiss constants θ_{ex} due to exchange alone [9]. For all three materials, $\theta_{ex} \cong -1$ mK. This is small compared to the ordering temperatures, which are approximately 30 mK (Dy), 21 mK (Gd), and 17 mK (Er). Thus these materials are extremely good approximations to an ideal dipolar system. Single crystals were recrystallized in water solution from 99.9% reagents. Powder x-ray diffraction patterns obtained at 10 K show no change in crystal symmetry from O_h^7 .

Static susceptibilities were measured in single crystal samples of approximately ellipsoidal shape, coated with vaseline to prevent loss of water of hydration. They were cooled inside the mixing chamber of a dilution refrigerator in fields of 0.5 and 0.05 mT. These fields are well below the classical critical field [1] for these materials, which is of order 10 mT. Thermal contact between samples and bath was surprisingly good. Powdered, uncoated samples cooled in the same apparatus exhibited the same ordering temperatures. Magnetization was measured using flux gate magnetometers, and sample temperature was measured by a CMN thermometer next to the samples inside the mixing chamber.

The low temperature static susceptibility per unit volume, corrected for demagnetizing field, is shown as a function of T in Fig. 2. All three compounds show a fairly sharp ordering feature, below which the susceptibility is nearly constant. Within experimental uncertainty, the susceptibilities were also isotropic. These features are qualitatively consistent with those expected for a classical dipolar antiferromagnet. The susceptibilities below T_c are very different in magnitude, however, in disagreement with Eq. (2).

From the paramagnetic Curie constant, the ground state of Er^{3+} in the phosphomolybdate structure is a doublet Γ_7 with a theoretical $g=6.8$, corresponding to an effective spin of $\frac{1}{2}$. Dy^{3+} has a quadruplet Γ_8 ground state, corresponding to effective spin $\frac{3}{2}$, with splitting parameters [10] satisfying $P^2 + Q^2 = 28.35 \pm 1$. This is very close to values measured for ${}^6H_{15/2}$ ions in a variety of other cubic environments [11–14]. The ground state of Gd^{3+} is not known, but the susceptibility is consistent

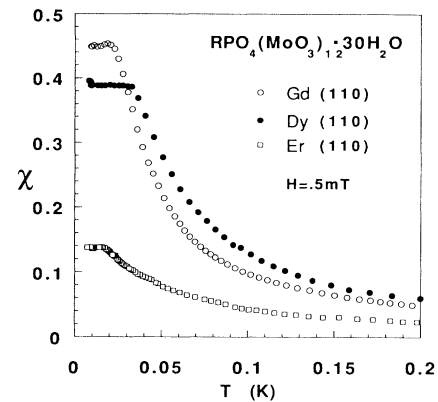


FIG. 2. Magnetic susceptibility per unit volume (dimensionless) as a function of temperature in three rare earth phosphomolybdates with diamond structure, corrected for demagnetizing field. Sample masses are 0.2008g (Gd), 0.0676g (Dy), and 0.0834g (Er).

with $S = \frac{7}{2}$ down to the ordering temperature. This is similar to the situation in fcc dipolar Gd compounds [3].

When the susceptibilities of Fig. 2 in the zero temperature limit are plotted as a function of $1/S$, where S is the effective spin, a nearly linear plot results, shown in Fig. 3. The error bars are due primarily to uncertainty in the sample demagnetizing factors. This is the behavior expected of an antiferromagnet with unusually large quantum spin fluctuations, expressed by the spin wave result [15]

$$\chi_{\perp}(T=0) = \chi_{\perp}^0 (1 - \Delta S/S - \Delta E/2E_0). \quad (3)$$

Here χ_{\perp}^0 is the classical Néel state susceptibility of Eq. (1). $\Delta S/S$ and $\Delta E/E_0$ are the sublattice spin reduction and ground state energy shift due to quantum zero-point motion, both proportional to $1/S$. From the least-squares slope of the line, we obtain $\Delta S/S + \Delta E/2E_0 = (0.36 \pm 0.04)/S$. The smallest susceptibility, for Er ($S = \frac{1}{2}$), is reduced by more than 50% from the largest (Gd), due to fluctuations. This substantially exceeds the fluctuations predicted for the nearest-neighbor Heisenberg antiferromagnet in three dimensions. The Heisenberg prediction for $\Delta S/S + \Delta E/2E_0$ in the sc lattice, for example, is $0.127/S$ [16]; for the diamond lattice, $0.192/S$. The intercept of the line at $1/S=0$ corresponds to the classical limit. It has a value $\chi(1/S=0) = 0.48 \pm 0.15$, which is not far removed from the theoretical expectation, $\chi_{\perp}^0 = (\lambda - 4\pi/3)^{-1} = 0.453$. This agreement is probably fortuitous, since the uncertainty associated with the sample demagnetizing factors ($\pm 30\%$) is larger than the difference between theory and experiment. The slope of the line in Fig. 3, and hence the magnitude of the zero-point motion, is much less sensitive to this uncertainty. It seems clear that there exist large quantum spin-fluctuation effects in these materials, and by inference, probably in other cubic dipolar magnets.

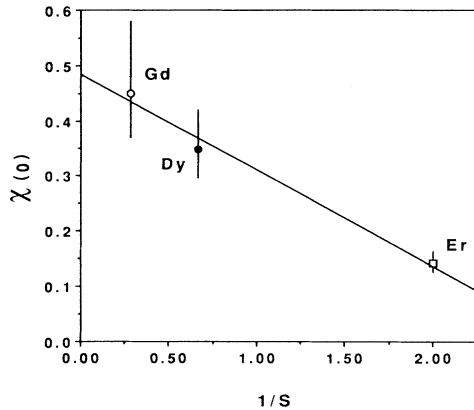


FIG. 3. Experimental susceptibility extrapolated to $T=0$, plotted as a function of $1/S$, showing the large effect of quantum spin fluctuations.

The substitution of ions with different S into the phosphomolybdate structure thus provides an unusual direct measurement of quantum spin fluctuations in a thermodynamic quantity, effectively at $T=0$. In exchange-coupled systems, this is ordinarily not possible, because the susceptibility depends additionally on the exchange constant J , and S cannot be varied without changing J as well.

The magnitude of the spin fluctuations agrees rather well with a spin wave calculation. Assuming the classical Néel state above, we obtain the dipolar spin wave spectrum of diamond by numerical diagonalization of the 8×8 matrix Hamiltonian, for a representative set of k . It is shown in Fig. 4. The tetragonal Brillouin zone corresponds to the unit cell of Fig. 1. The spectrum has four branches, with a zero in one branch at the zone center. A second branch shows the nonuniform convergence at $k=0$ characteristic of dipolar antiferromagnetism [17]. The ground state energy in this approximation is

$$E_{\delta}^{\text{sw}} = E_0(1 + 1/S) + \frac{1}{2} \sum_{i=1}^4 \sum_k \omega_k^i = E_0(1 + \Delta E/E_0), \quad (4)$$

where ω_k^i is the spin wave energy in branch i . A numerical evaluation of the sum yields a zero-point motion term $(\Delta E/E_0)_{\text{dia}} = 0.231/S$. This result is nearly identical to that previously calculated for the simple cubic dipolar lattice, $(\Delta E/E_0)_{\text{sc}} = 0.236/S$ [17]. For comparison, the corresponding value for the nearest-neighbor Heisenberg antiferromagnet on a diamond lattice is $\gamma_{\text{dia}}/zS = 0.147/S$. The sublattice spin reduction is similarly large. We obtain $\Delta S_{\text{dia}} = 0.224$, a 45% reduction for $S = \frac{1}{2}$. This is nearly twice the Heisenberg result, $\Delta S_{\text{dia}}(\text{Heis}) = 0.118$, but close to that for dipolar sc, $\Delta S_{\text{sc}} = 0.252$. The unusual size of the dipolar spin fluctuations may be related to the fact that the total magnetization M_z is not a conserved quantity, as it is in the isotropic Heisenberg model. From these results we calculate the susceptibility at $T=0$

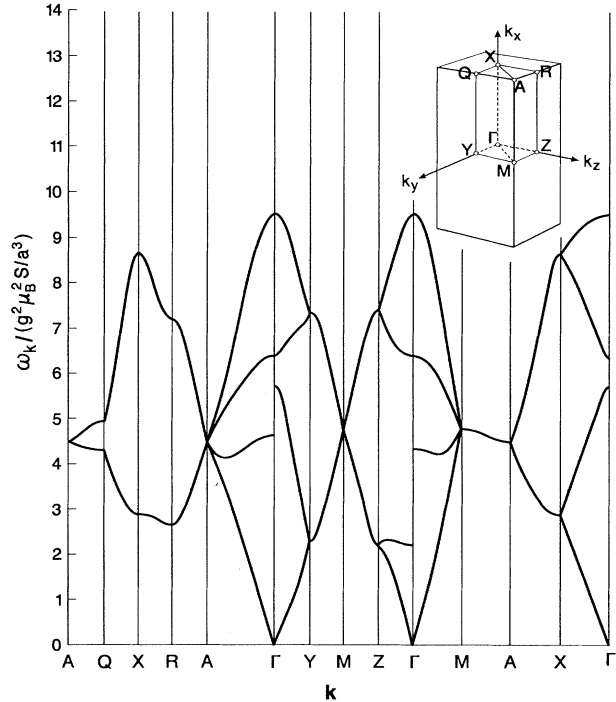


FIG. 4. Calculated dipolar spin wave spectrum for diamond. One branch is gapless at the zone center; another shows nonuniform convergence there. The diamond cube edge equals $2a$.

to be [from Eq. (3)]

$$\chi_{\perp}^{\text{dia}}(T=0) = \chi_{\perp}^0(1 - 0.340/S). \quad (5)$$

The fluctuation term $0.340/S$ agrees within experimental error with the measured slope in Fig. 3, $(0.36 \pm 0.04)/S$.

A calculation of χ_{\parallel} yields

$$\chi_{\parallel}^{\text{dia}}(T=0) = -\frac{1}{2V} \frac{\partial^2}{\partial H^2} \sum_i \sum_k \omega_k^i = 0.031/S. \quad (6)$$

While it is roughly an order of magnitude smaller than $\chi_{\perp}(0)$, it is not zero, as it is in the Heisenberg antiferromagnet. The difference is due to the nonconservation of M_z for the dipolar Hamiltonian.

These results should be relatively insensitive to the presence of a small residual exchange interaction. The effect of exchange is largest on low-lying excitations, where it might be expected to open up a gap in the spin wave spectrum. This will not happen in the case of the diamond lattice, however, because its spectrum goes to zero at the zone center, just as the exchange spectrum does.

In nuclear dipolar systems studied by NMR, such as CaF_2 , these effects are reduced by approximately an order of magnitude. In such experiments, the dipolar Hamiltonian is a perturbation compared to the larger Zeeman energy. The effective Hamiltonian is not the full dipolar Hamiltonian, but only the part of it which commutes with

the Zeeman energy [18]. This "truncated" dipolar Hamiltonian does not have all the symmetries of the original version, and has a large gap in its spin wave spectrum [19]. The gap leads to very small spin-fluctuation effects and nearly classical behavior.

Ferromagnetic order is expected to lead to qualitatively similar temperature dependence of the experimental susceptibility $\chi_{\text{exp}} = M/H_{\text{ext}}$. However, its value below T_c is equal simply to the inverse of the sample demagnetizing factor, and has no dependence on S [20]. The presence of quantum fluctuations is masked by the motion of domain walls. For this reason, the observed susceptibilities of the rare earth phosphomolybdates are consistent with antiferromagnetic order, but not with ferromagnetism.

In summary, we have observed magnetic behavior in the rare earth phosphomolybdates which is consistent with dipolar antiferromagnetic order. Quantum spin fluctuations substantially exceeding those of exchange-coupled antiferromagnets are directly observable in the susceptibility. The magnitude of these fluctuations agrees well with theory. Dipolar magnets, commonly perceived as inherently more classical than those based on exchange, in fact appear to be just the opposite.

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