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Search for the Ground State of Cerous Magnesium Nitrate by an Extended Luttinger–Tisza Method

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The ground state of cerous magnesium nitrate is determined using the assumptions that the spins are coupled by purely dipolar forces, the magnetic structure is periodic after eight or less lattice periods, and the spins can be considered as classical vectors. The ground state has a layered antiferromagnetic structure as described in the text. A study is made to see whether this result is dependent on the assumption that the g factor parallel to the crystallographic c axis is zero or almost zero for this specific salt. The conclusion is that this is to a large extent not the case. The ground state lies at an energy -1.867 mdeg K, using the lattice constants as given by Schiferl.

INTRODUCTION

This paper describes the search for the ground state of a dipolar-coupled spin system beyond the simplest form of the Luttinger–Tisza calculation. Its main application is to cerous magnesium nitrate (CMN) which seems to be an almost pure dipole system. We also investigate the question of how our conclusions depend on the fact that in the case of this specific salt, the g factor in the c direction is practically zero. The search for the ground state of CMN is closely connected with questions concerning elementary excitations and critical behavior, since most theories for cooperative phenomena use a preconceived idea for the ground state. The long-range behavior of the dipole interaction makes it difficult to replace the interaction by an effective field and the strong angle dependence makes it difficult to decide whether the ground state is ferromagnetic or antiferromagnetic. The ground state can, in general, be approximated by minimizing the coupling energy of a cluster but, given the long-range nature of the forces, the cluster would have to be quite large in order to obtain a good approximation. In order to describe infinite crystals one usually makes use of periodic boundary conditions. The method of Luttinger and Tisza[1] is a combination of these two ideas: a cluster that is periodically repeated. The spins in the cluster consequently interact not only with the other members of the cluster, but also with spins at much larger distances; however, owing to the imposed periodicity, the dimensionality of the matrix, that has to be diagonalized eventually, is greatly reduced. A further simplification is obtained by replacing the spins by classical vectors, as well as a relaxation of the constraint that the individual lengths of the spins should be conserved. The gist of the Luttinger–Tisza method is the assumption that a cluster of eight spins ($2 \times 2 \times 2$) is considered to be identical within each periodically repeated cluster. This superlattice structure was

introduced to take the long range (actually the dipole forces have an infinite range) into account, without having to solve the total N-body problem.

Previous work consists of the calculation of Luttinger and Tisza[1], which was the first attempt to obtain the ground state of dipolar systems in general. There were several more attempts.[2] Finally, there is a paper specifically devoted to CMN by Daniels and Felsteiner[3] and a paper by Niemeijer[4] which gives an analytic solution to the Luttinger–Tisza procedure for a $2 \times 2 \times 2$ basic cluster with an application to CMN, including a variable exchange interaction between nearest neighbors.

The last two papers can be used to argue that the ground state of the spin system of CMN is antiferromagnetic, which it well may be. It was shown, however, in Ref. 4 that the Luttinger–Tisza method, using a $2 \times 2 \times 2$ basic cluster, is rather restrictive since it can give but two answers: The system can be either ferromagnetic or antiferromagnetic (although there are several antiferromagnetic structures possible). Since nature obviously provides us with a much larger number of options, the question arises whether one can loosen one of the major restrictions of the calculation, namely, by choosing a larger superlattice, and hence obtaining more possible arrays than in Ref. 4. We introduce the expressions "weak" and "strong" following Ref. 1. The strong condition means that all spins have a fixed length, the weak (also called "spherical") condition means that only the total spin has a fixed length. If we take a $2 \times 2 \times 2$ cluster, it was proved in Ref. 4 that the weak condition automatically implies the strong condition, but if we take an $N \times N \times N$ basic cluster, with $N = 2, 3, 4, \ldots$, the extended number of possible arrangements need no longer fulfill the strong condition if the weak condition is used in determining the ground state. This means that if one determines the lowest eigenvalue of the pertaining $3N^3 \times 3N^3$ matrix, one should always check whether the corresponding eigenvector satisfies the strong constraint, i.e., corresponds to a physically permissible situation. Since this does not need to be so for $N > 2$, the extrapolation of this procedure to larger superlattices does not necessarily lead to the actual ground state.

We have applied the Luttinger–Tisza method with $N = 3, 4, \ldots, 8$ to CMN and neodymium magnesium nitrate (NMN). All lattice sums were taken over all points inside a sphere. The size of the sphere was chosen to be proportional to the size of the superlattice. The actual method of computing the lattice sums has been described by Meijer and O'Keeffe.[5]

SYMMETRIES

The "interaction matrix" is of dimension $3N^3$, where N is the number of steps in the superlattice. We consider for the moment a matrix of dimension N^3 made up of 3×3 matrices as elements. This matrix consists of rows (columns) that can be considered as permutations of a given row (column). This is the result of the fact that the relative distances between certain pairs of lattice points are equal both in length and in orientation. For low-N values this can be done by visual inspection of a three-dimensional picture. Since this gets tedious in the long run, we designed a little algorithm, suited for the computer.

If we take, for example, the case $N = 2$, we have eight points, labeled 1 – 8. This label number minus 1 can be considered as base-2 numbers: 000, 001, 010, 011, 100, 101, 110, 111, and these digits can be interpreted as the integers in front of the basic translation vectors a, b, and c. (In fact, this seems to be exactly the choice Daniels and Felsteiner used in their Fig. 1.) The distance between two given locations L and L' is always equal to a distance from the origin to a point L''. To determine L'' for given L and L' one subtracts the numbers, digit by digit, and considers them modulo N, if they are negative. The label L'' is the result rewritten on base 10, plus 1. The result is, for $N = 2$, the following matrix:

1	2	3	4	5	6	7	8
2	1	4	3	6	5	8	7
3	4	1	2	7	8	5	6
4	3	2	1	8	7	6	5
5	6	7	8	1	2	3	4
6	5	8	7	2	1	4	3
7	8	5	6	3	4	1	2
8	7	6	5	4	3	2	1

The general procedure is as follows. The label L of the N^3 points that make up the unit cell in the $N \times N \times N$ superlattice is written as a base-N number, by taking the integer values

$$n_1 = [N^{-2}(L-1)],$$

$$n_2 = [N^{-1}(L - 1 - n_1 N^2],$$

and

$$n_3 = L - 1 - n_1 N^2 - n_2 N.$$

The relative distance between two points L and L' is equal to the distance between L'' and the origin, where L'' is given by $n_1'' N^2 + n_2'' N + n_3'' + 1$, where $n_i'' = \text{mod}\,(n_i - n_i')$ for $i = 1, 2, 3$. The resulting table has the following property. Each column (row) is a permutation of another column (row). Let us take the first column in the order 1, N^3; then we find the others by operating with the following permutation operators:

$$P_2 = (1,\ 2,\ \ldots,\ N)\ (N+1,\ \ldots\ 2N)$$

$$\ldots\ (\textstyle\sum[(N^2-1)N+1],\ \ldots,\ N^3)\ ,$$

as well as by those that have a similar structure, namely, N^2 cycles of length N. To write the numbers in each cycle one may use the same method as was used in the computer algorithm: Each label equals 1 plus a three-digit base-N number, and one should cycle each of the digits independently. When the pertaining lattice sums have been performed for a special choice of N, the effective Hamiltonian of the basic cluster can be written as

$$\mathcal{H} = \sum_{\vec{R},\vec{R}'} \sum_{\alpha,\beta=x,y,z} J^{\alpha\beta}_{\vec{R},\vec{R}'} S^{\alpha}_{\vec{R}}\, S^{\beta}_{\vec{R}'}\ ,$$

where $\vec{R}$ and $\vec{R}'$ run over the basic cluster and $S^{\alpha}_{\vec{R}}$ ($\alpha = x,\ y,\ z$) are the Pauli spin operators of the spin at site $\vec{R}$. The matrices $J_{\vec{R},\vec{R}'}$ are translationally invariant, i.e., depend only on $\vec{R}-\vec{R}'$, and so can be broken up in 3×3 matrices, since α and β still run over x, y, and z, by a Fourier transformation

$$A^{\alpha\beta}_{k_1,k_2,k_3} = \sum_{\vec{R}} A^{\alpha\beta}_{\vec{R}} \exp\left(\frac{2\pi i}{N}\,(k_1 n_1 + k_2 n_2 + k_3 n_3)\right),$$

where the set of integers $(n_1,\ n_2,\ n_3)$ is labeled $\vec{R}$, and k_1, k_2, and k_3 take on the values $0,\ 1,\ \ldots, N-1$. This result was already observed by Lax[6] in his paper on the spherical model of classical dipoles on a lattice. Indeed, the weak constraint is another name for sphericalization. The procedure of the paper actually consists in selecting a subset of spherical-model eigenvalues, examining the lowest, and ascertaining that the state corresponding to the lowest eigenvalue obeys the strong constraint. The expression above was computed for all N^3 cases and the set of three-dimensional matrices diagonalized one after another. At the same time the eigenvalues were determined.

RESULTS

In each set of $3N^3$ eigenvalues one looks for the lowest and the next lowest. The result of the computations for CMN is given in Table I. Note that the values given are in millidegrees. To check our computations we first inserted the lattice constants used in Ref. 3; the results are obtained by using Schiferl's[7] low-temperature values. It turns out that all eigenvalues correspond to $(0, 0, \frac{1}{2}n)$ ($n = 1,\ 2,\ \ldots, N$) in k space, for N even. These values are always degenerate with $(0,\ \frac{1}{2}n,\ 0)$ and $(\frac{1}{2}n,\ 0, 0)$. This property is the consequence of the symmetry of the lattice in k space.

For odd values of N we find that the lowest eigenvalue is obtained for $(0, 0,\ \frac{1}{2}(n\pm 1))$ and its two counterparts $(0,\ \frac{1}{2}(n\pm 1),\ 0)$ and $(\frac{1}{2}(n\pm 1))$. The $\pm$ sign refers to two states that are identical, since they differ by n. While the previous set of states, for even n, did obey both the strong and the weak constraint, these states do only fulfill the weak constraint.

TABLE I. Lowest eigenvalue in mdeg for superlattices sizes N for cerous magnesium nitrate using $a = 10.9857$ Å, $c = 17.034$ Å (Ref. 7), $g_\perp = 1.828$, and $g_\parallel = 0.032$.

N	Lowest energy	Corresponding k value
2	−1.915	(0, 0, 1)
3	−1.862	(0, 0, 1)
4	−1.916	(0, 0, 2)
5	−1.896	(0, 0, 2)
6	−1.916	(0, 0, 3)
7	−1.906	(0, 0, 3)
8	−1.917	(0, 0, 4)

The main conclusion of the table is that the antiferromagnetic state seems to be always the lowest, since one finds (almost) the same value for the lowest eigenvalue for $(0, 0, \frac{1}{2}n)$ for each even N. Hence this state, which in the previous calculations was just one choice out of eight, persists even if one has *a priori* the choice out of 512 possibilities. If we compare (0, 0, 1) for $N = 2$, with (0, 0, 2) for $N = 4$ and (0, 0, 4) for $N = 8$, we find a slight lowering of the eigenvalue. This is mainly due to the finite radius $R = 6$ a units (the lattice constant in the plane), which we had to choose in order to keep the $N = 8$ run within reasonable time limits. Admittedly, this radius is not very large; in order to obtain an idea about the error we made runs with $R = 3$ and the answers changed by less than 1% for $N = 4$. Since in the larger-N values the number of points participating in the sum is much larger (about 5000 lattice points), we obtain a more accurate result for the eigenvalue.

Some attention should be given to the states somewhat higher than the ground state, since the energy differences are rather small. One such state is, for instance, (0, 0, 2) for $N = 5$ or (0, 0, 1) for $N = 3$. Such states are associated with spin structures that can be described by the same antiferromagnetic planes as were used by Daniels and Felsteiner,[3] but the orientation of each sucessive plane is rotated over a certain angle ($\frac{4}{5}\pi$ or $\frac{2}{3}\pi$). If these were possible states, then this result would give an indication that the coupling *between* the planes would be rather loose. It is obvious, however, that these states do not satisfy the strong constraint, and if a similar state obeying the strong condition does exist, it may either have a much higher energy and the coupling between the planes is not so weak or, if the energy is not that much higher, the previous conclusion that the coupling between the planes is weak stands as before. The only way we can determine whether the strong constraint will increase the en-

ergy considerably is to do a complete quantum-mechanical calculation. This issue is of importance as soon as we begin to develop a spin-wave theory, since another set of low-lying levels will affect the calculations. We have repeated the same calculations for NMN, assuming that it has the same lattice constants as CMN (which is reasonable, since LaMN is known to have practically the same lattice constants as CMN). The g factors of the Nd ions are $g_\perp = 2.72$ and $g_\parallel = 0.45$. The results are given in Table II.

As can be seen, we have in principle the same situation as for CMN; i.e., the ground-state configuration found with $N=8$ is the same as the ground state configuration found with $N=2$ and $N=4$. The slight variation in the energies is due to the fact that we have used $R=3$ for all values of N. It appears that the ground-state configuration is exactly equal to that of CMN, which means that the fact that we have now $g_\parallel = 0.45$ instead of zero has no influence. These results indicate that the true classical ground state for CMN as well as NMN probably is the state obtained with $N=2$ and $k = (0, 0, 1)$, and one might speculate this to be a general property of classical systems of dipoles on a Bravais lattice.

To see what would be the influence of a larger change of $g_\parallel$ we have determined the ground state for a number of values of $\gamma = g_\parallel/g_\perp$ in the range $0 \cong \gamma \cong 1.6$. It is found that for $0 \cong \gamma \lesssim 0.85$, the ground state is exactly the same as that of CMN. For $0.85 \lesssim \gamma \lesssim 0.98$ there is a different sublattice structure with parallel spins on lattice sites 1, 2, 7, and 8 and antiparallel ones as lattice sites 3 – 6 (see Ref. 4 for the labeling of the lattice sites). For $0.98 \lesssim \gamma \lesssim 1.6$ one again has the same sublattice structure as for CMN, but now the spins lie in the y-z plane (see Note added in proof).

A paper giving a quantum-mechanical extension of the Luttinger–Tisza method is in preparation.

TABLE II. Lowest-eigenvalue for neodymium magnesium nitrate (isotope without nuclear spin) with the same lattice constants and $g_\perp = 2.72$ and $g_\parallel = 0.45$.

N	Lowest energy	Corresponding k value
2	−4.237	(0, 0, 1)
3	−4.119	(0, 0, 1)
4	−4.240	(0, 0, 2)
5	−4.194	(0, 0, 2)
6	−4.239	(0, 0, 3)
7	−4.217	(0, 0, 3)
8	−4.241	(0, 0, 4)

SHAPE DEPENDENCE

The interaction energy in a dipolar system is dependent on the shape of the sample. This is due to the fact that the summation over the dipole interaction is a conditionally convergent summation; that is, if the summation were to be extended to infinity, the result would depend on the order of the summation. In this case we utilize a finite summation inside a sphere of radius about $6Na$, as indicated above. The length a is the distance between two cerium atoms in the plane perpendicular to the z axis. We assume that beyond this distance the contribution to the sum is equal to the contribution of a continuous dipole distribution, which is zero if (a) the sample has the same shape as the surface beyond which the distribution was considered to be continuous (that is, since the surface was chosen to be a sphere, the sample should also be a sphere) and (b) the summation sphere lies inside the sample. Those spheres that do not fulfill this last condition lie in the surface layer. The volume of the surface layer can always be considered small compared to the volume of the remaining part of the sample.

The above argument no longer holds if the sample is not homogeneously magnetized but breaks up in domains. In the ferromagnetic case we will have an additional contribution to the energy. It was already shown, however, in Ref. 2 (pp. 290 and 291) that the energy of the ferromagnetic state is lowered in this way, but that it still lies *above* the energy of the antiferromagnetic state. This holds, of course, irrespective of the size of the basic unit cell and we conclude that the ground state is antiferromagnetic.

Note added in proof. We found that, looking at 004, etc., the matrix $A^{\alpha\beta}$ has only two off-diagonal elements that are nonzero: $A^{yz} = A^{zy} \neq 0$ and that the lowest eigenvalue is given by A^{xx}. Increase of the $g_\parallel$ factor will increase both A^{zz} and the nonzero off-diagonal matrix elements. This increase will spread the two coupled eigenvalues apart, without affecting the A^{xx}. At a certain moment there will be a crossing and the A^{xx} is no longer the lowest.

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Polarized-Neutron Study of the Induced Magnetic Moment in TmSb†

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The magnetic form factor of the induced moment in TmSb has been measured with polarized neutrons. Thulium antimonide is a singlet-ground-state system, i.e., it has no spontaneous magnetic moment, but under the conditions of the experiment the magnetization develops through the mixing of the ground state with the first excited state. The experiments were performed on a single crystal at 5 °K and an applied field of 12.5 kOe. Measurements were taken with $\vec{H} \parallel \langle 100 \rangle$ and $\vec{H} \parallel \langle 110 \rangle$. The theoretical magnetic form factor has been derived using the tensor-operator technique of Johnston, Lovesey, and Rimmer, and the nonrelativistic wave functions of Freeman and Watson. The experimental form factor with $\vec{H} \parallel \langle 100 \rangle$ is essentially a smooth curve as a function of $\sin\theta/\lambda$, while for $\vec{H} \parallel \langle 110 \rangle$ considerable anisotropy is observed at high scattering angles. This anisotropy arises from the nature of the ground state and is determined by the crystal field acting on the rare-earth ion. The present technique may therefore be useful in investigating the ground states of the many compounds with unquenched orbital moments and appreciable crystal field interactions. The experimentally observed anisotropy is in complete agreement with theory. Previous polarized-neutron experiments on rare-earth metals indicate that the spatial extent of the $4f$ electrons is more expanded than given by the nonrelativistic calculations. The observed form factor in TmSb does not agree with the form factor calculated with nonrelativistic wave functions. Good agreement is obtained by using the $4f$ radial distribution as determined from polarized-neutron measurements on thulium metal. A set of $\langle r^n \rangle$ integrals has been derived from the experimental radial densities.

I. INTRODUCTION

Over the last three years the polarized-neutron technique has been used successfully to measure the magnetic form factors of the heavy rare-earth metals gadolinium,[1] thulium,[2] and terbium.[3] These measurements indicate a major discrepancy between the experimentally deduced spatial density of the $4f$ electrons and that calculated with nonrelativistic wave functions.[4] The advent of relativistic calculations[5,6] appears to remove at least some of this discrepancy, although the problem of understanding the conduction-electron polarization still remains. In addition, measurements on the ionic system Gd_2O_3[1] indicate an unexpected agreement with the form factor derived from nonrelativistic wave functions. The rare-earth pnictides have been extensively studied recently, and the metallic compound TmSb (NaCl structure, $a_0 = 6.076$ Å) provides an excellent candidate for a polarized-neutron investigation for the following reasons: (a) Very accurate single-crystal magnetization experiments have been performed on TmSb by Cooper and Vogt,[7] and Foner *et al.*,[8] and used to derive the crystal field parameters. Additional magnetization experiments[7] on the $Tm_xY_{1-x}Sb$ system indicate that the exchange is negligible in TmSb. The results of Cooper and Vogt show that TmSb is a singlet-ground-state system, and that the induced moment at 4.2 °K is isotropic in fields less than 15 kOe. Inelastic-neutron measurements[9] have further refined the crystal field parameters, confirming the model proposed by Cooper and Vogt. (b) From an experimental point of view, TmSb is ideal for accurate form-factor measurements since a magnetic moment of $\sim 1\mu_B$ per Tm atom can be induced with a field ~ 10 kOe at helium temperature. (c) Polarized-beam measurements have been reported on thulium metal[2] and a comparison of the $4f$ electron wave functions in the two environments can be made.

The theoretical calculation of the magnetic form factor is also of interest since this is a singlet-ground-state system without exchange, and the form