

Quantum-mechanical ground state of cerous magnesium nitrate

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This paper deals with the quantum-mechanical ground state of cerous magnesium nitrate (CMN). The approximation used is that of Luttinger and Tisza and of Niemeijer, in which spin correlations for magnetic ions in the same supercell are taken into account, while those between ions in different supercells are neglected. The method used is that presented in an earlier paper of the present authors. It is found that the quantum-mechanical ground state of CMN is a linear combination of the state with spin orientations those of the classical state found by Niemeijer plus the complementary state. Thus the classical state is a good approximation for quick results. This state has nearly the same energy as the three mutually degenerate states belonging to the \vec{k}_1 , \vec{k}_2 , and \vec{k}_3 representations of the translation group. These are formed by linear combinations of states with four spins up and four spins down as is the case with the ground state. The results found fit well with the existing experimental information about CMN.

I. INTRODUCTION

In this paper the theory developed in the preceding paper, referred to as I,¹ is applied on the typical paramagnetic crystal of $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12}\cdot 24\text{H}_2\text{O}$ (CMN). The paramagnetic behavior of CMN is due to the fact that there are three types of dipole-dipole interactions, i.e., the interaction between Ce^{3+} ions, between Ce^{3+} and protons (nucleons of the water molecules), and between protons.² The coupling constant for the first interaction is much greater than those of the two other interactions.³ Thus the experimentally found transition temperature 1.8 mK is due to the dipole-dipole interaction of Ce^{3+} ions.⁴ In higher temperatures the crystal has paramagnetic behavior, but in lower temperatures the system of Ce^{3+} ions is in its ground state while the proton susceptibility obeys the $1/T$ law because its interaction with Ce^{3+} ions is very weak. The transition temperature of the protons, which is related to the proton- Ce^{3+} interaction, is about 3 orders of magnitude below 1.8 mK, which is the transition temperature of the cerium-ion system. Thus it is clear that the interaction between the Ce^{3+} ions is the most significant. The spin of Ce^{3+} is $\frac{1}{2}$.³⁻⁶

The experimental results of Abeshouse, Zimmerman, Kelland, and Maxwell⁶ and also of Fisher, Hornung, Brodale, and Giauque⁵ suggest that the ground state of CMN is antiferromagnetic. They do not, however, agree with the experimental results of Mess, Lubbers, Niesen, and Huiskamp.⁴ All recent experimental evidence shows that CMN is antifer-

romagnetic in its ground state.^{5,6}

Many scientists dealt with the ground state of CMN theoretically. Daniels and Felsteiner⁷ and Felsteiner and Friedman,⁸ who used the method of Luttinger and Tisza, derived an antiferromagnetic ground state. Niemeijer's results derived by the application of the "semiclassical" theory agree with the above.³

The quantum-mechanical treatment of the problem by Niemeijer and Meijer gives similar results.⁹⁻¹¹ The application of our theory to CMN shows also that CMN is in an antiferromagnetic ground state, as one can see in the last section of this paper. The difference between our results and those of Meijer and Niemeijer¹¹ is that we have calculated with sufficient accuracy in the case of CMN the energies of the eigenstates by using only the general approximation used in these cases about the form of the wave functions $|\Psi\rangle$ (Ref. 1) because our correction term, for CMN, comes out identically zero. The Meijer and Niemeijer result does not agree with our form of the wave function. Also, their final result for the ground-state energies is very different from ours as well as from Niemeijer's classical theory. This disagreement is discussed in Sec. V.

Section II of this paper deals with the Hamiltonian of CMN in the representation discussed in paper I. In Sec. III we discuss the effect of the correction term. In Sec. IV the energy and magnetization of the eigenstates derived from our theory are presented. In Sec. V, the general conclusions are discussed and compared with the theoretical and experimental results.

II. THE HAMILTONIAN OF CMN

The Hamiltonian of the system of Ce ions of the dipolar crystal CMN is the typical dipole-dipole interaction Hamiltonian¹²

$$H_0 = \frac{1}{2} \sum_{i,j} \frac{1}{R_{ij}^3} \left[\vec{\mu}_i \cdot \vec{\mu}_j - 3 \frac{(\vec{\mu}_i \cdot \vec{R}_{ij})(\vec{\mu}_j \cdot \vec{R}_{ij})}{R_{ij}^2} \right]. \quad (1)$$

The Niemeijer approximations^{3,11} that the expectation value of spin has twice the periodicity of the cerium-ion lattice, with the additional assumptions of the preceding paper¹ that there is no correlation between the spins of the same sublattice and that the correlation between spins of a different sublattice is independent of the exact site of the spin, leads to the following Hamiltonian:

$$H_0 = \frac{1}{2} \sum_{\vec{R}, \vec{R}'} A_{\vec{R}, \vec{R}'}^{\alpha\beta} S_{\vec{R}}^{\alpha} S_{\vec{R}'}^{\beta} + \frac{1}{2} \sum_{\vec{R}} A_{\vec{R}, \vec{R}}^{\alpha\beta} \langle \Psi | S_{\vec{R}}^{\alpha} | \Psi \rangle S_{\vec{R}}^{\beta}. \quad (2)$$

The eigenvalues of H_0 are the expectation values of the energy per ion.¹ Because of the nonlinearity of the second term of the Hamiltonian H_0 , we treat it as a correction term as discussed analytically in the preceding paper.¹ The quantities $A_{\vec{R}, \vec{R}'}^{\alpha\beta}$, which are elements of a matrix A , are defined in Refs. 3 and 12.

By using group-theoretical methods one can show that the first term of the Hamiltonian H_0 , i.e., the Hamiltonian with the correction term omitted, can be written¹

$$H_0' = \frac{1}{16} \sum_{\vec{k}, l} \lambda_{\vec{k}}^l \left[\sum_{\alpha=x,y,z} \varphi_{\vec{k}, l}^{\alpha} b_{\vec{k}}^{\alpha} \right]^2. \quad (3)$$

The quantities $\lambda_{\vec{k}}^l$ are the eigenvalues of the matrix A , and their definition and values in the case of CMN are given in Refs. 3 and 12. The quantities $\varphi_{\vec{k}, l}^{\alpha}$ are the components of the directional part of the eigenvectors of A .^{3,12}

In the preceding paper¹ we dealt with the method of solution. The basis we chose is the same as that of Meijer and Niemeijer¹¹ apart from notation and the choice of quantization axis. In this paper the x axis of the crystal was chosen as quantization axis instead of the z axis chosen in Ref. 11. The appropriate definition of the basis of the space enabled us to avoid the difficult problem of diagonalizing a 256×256 matrix. Instead we must diagonalize

several matrices of dimensions 30×30 and one matrix of dimension 46×46 . The last is the matrix of the identity representation. In addition to the numerical simplification, one gets more physical insight into the problem by the method adopted in this paper. It must be noted that we have used only the general translational symmetry of the lattice. The full spatial symmetry of the cerium-ion lattice of CMN,² which can be derived by using the D_{3d} symmetry of the unit cell, was used as a check of our calculations.

III. THE CORRECTION TERM

The correction term of the energy defined in the preceding paper,¹ which by means of the eigenstates of H_0' gives the eigenvalues of H_0 by first-order perturbation theory, has a simple form in the case of CMN.

Because of the fact that $g_z = 0$ (Refs. 3 and 13) in CMN, only terms which involve the quantities $A_{\vec{R}, \vec{R}'}^{xy}$, $A_{\vec{R}, \vec{R}'}^{yz}$ and $A_{\vec{R}, \vec{R}'}^{zx}$ appear in the Hamiltonian of the system.³ However, the element $A_{\vec{R}, \vec{R}'}^{xy}$ is zero for CMN. Then the form of the correction term, after taking into account that $A_{\vec{R}, \vec{R}'}^{\alpha\alpha}$ is independent of \vec{R} and $\langle S_{\vec{R}}^{\alpha} \rangle^2 = \frac{1}{4}$, is

$$E_c(|\chi_{\vec{k}}\rangle) = \frac{1}{2} \sum_{\alpha=x,y} A_{0,0}^{\alpha\alpha} (\langle \chi_{\vec{k}} | b_0^{\alpha} | \chi_{\vec{k}} \rangle)^2 - \sum_{\alpha=x,y} A_{0,0}^{\alpha\alpha}. \quad (4)$$

The term $\sum_{\alpha=x,y} A_{0,0}^{\alpha\alpha}$ does not change the eigenstates of H_0' , but it increases by the same quantity all the eigenvalues of H_0' . The other part of the correction term can be written as a function of the magnetization of the crystal and can be calculated by means of the eigenstate $|\chi_{\vec{k}}\rangle$.¹

In fact, in the case of CMN, because $g_{\alpha\beta} = g_{\alpha} \delta_{\alpha\beta}$, $g_z = 0$, and $g_{\alpha} = g_{\beta} = g_1$,^{3,13} the magnetization per cluster can be expressed as

$$M^{\alpha} = m_B g_1 \langle \chi_{\vec{k}} | b_0^{\alpha} | \chi_{\vec{k}} \rangle, \quad \alpha = x, y. \quad (5)$$

From Eq. (4) the final form of the correction term is

$$E_c(|\chi_{\vec{k}}\rangle) = \frac{1}{16 m_B^2 g^2} \sum_{\alpha=x,y} A_{0,0}^{\alpha\alpha} (M^{\alpha})^2 \sum_{\alpha=x,y} A_{0,0}^{\alpha\alpha}. \quad (6)$$

The quantity $-\sum A_{0,0}^{\alpha\alpha}$ has the value -0.269 mK. Thus we must raise all eigenvalues of H_0' by -0.269 mK. For the other part we can make an estimate by calculating its maximum value.

Because the quantities $A_{0,0}^{xx}$ and $A_{0,0}^{yy}$ are equal,³ the maximum value of the correction is defined by

the maximum value of $M^x^2 + M^y^2$, which is the square of the magnetization, with maximum value $16m_B^2g_1^2$, when $|\chi_{\vec{k}}\rangle$ is the vacuum or the full state¹ (see the preceding paper). Thus the maximum value of the significant part is 0.135 mK, which when added to the value of $-\sum A_{00}^{\alpha\alpha}$ gives -0.134 , mK, which is much smaller than the value of the ground state, which is -16.59 mK.

IV. THE GROUND STATE AND THE EXCITED STATES

Having the appropriate basis and the action of the Hamiltonian on the basis from paper I, we can calculate the matrix elements of the Hamiltonian for this basis and diagonalize the resulting matrix. In this way one can find the eigenvalues and eigenstates of energy. Then it is easy to find directly the components of magnetization, and from Eq. (6) the correction term. The computation has been carried out by the use of the CDC 3.300 computer system of the Nuclear Research Center "Demokritos."

The results show that for any eigenstate of CMN the magnetization is zero. Thus the significant part of the correction term is zero, and the correct eigenvectors and eigenvalues of H_0 are those of H'_0 .

The eigenstates and eigenvalues are tabulated for the various irreducible representations of the translation group in Ref. 14.

V. DISCUSSION

According to the preceding section, the calculation of the eigenstates and the eigenvalues of H_0 from those of H'_0 does not introduce errors. The D_{3d} point symmetry of the crystal CMN suggests² that the eigenstates of CMN have various degeneracies. In fact, the states of the identity representation of the translation group will be singly or doubly degenerate. On the other hand, there exist degeneracies between the states of the \vec{k}_1 , \vec{k}_2 , and \vec{k}_3 representations and between the states of the \vec{k}'_1 , \vec{k}'_2 , and \vec{k}'_3 representations. The states of the \vec{k}_2 representation have the same behavior as those of the identity representation.^{1,12}

As one can see from Tables I–VIII (Ref. 14) the states of different representations found numerically are in agreement with the above results of group theory, and this confirms that our calculations are correct.

The ground state determined by using our method is doubly degenerate; it belongs to the identity representation and its energy is -16.59 mK. It is lower than the energy of the "semiclassical" ground state of Niemeijer, which has the value -15.001 mK, belongs to the \vec{k}_1 representation, and is degenerate to

the \vec{k}_2 and \vec{k}_3 representations.^{3,12}

The fact that the quantum-mechanical ground state has lower energy than the "semiclassical" ground state was expected because the space of the wave functions of the "semiclassical" method is a subspace of the quantum-mechanical space (see the Appendix). In fact, the quantum-mechanical method leads to Niemeijer's semiclassical ground state if one takes as the space of the Hamiltonian the subspace of the purely antiferromagnetic and ferromagnetic wave functions only. This is because the matrix elements of the operators that change the number of spins in this subspace will be zero. Because of some computational error Niemeijer and Meijer¹¹ have found in their quantum-mechanical treatment of the ground state of CMN greater energy than that of the "semiclassical" ground state.

As one can see from Table I,¹⁴ the main component of the ground state is the antiferromagnetic state $|\varphi_0(\vec{R}_2, \vec{R}_3, \vec{R}'_1)\rangle$. This state, according to its definition [Eq. (30) of Ref. 1] can be written analytically as

$$|\varphi_0(\vec{R}_2, \vec{R}_3, \vec{R}'_1)\rangle = \frac{1}{\sqrt{2}}(S_0^+ S_{\vec{R}_2}^+ S_{\vec{R}_3}^+ S_{\vec{R}'_1}^+ |0\rangle + S_{\vec{R}_2}^+ S_{\vec{R}_3}^+ S_{\vec{R}'_1}^+ |0\rangle), \quad (7)$$

i.e., it is a superposition of the state which has spin up at the sites $0, \vec{R}_2, \vec{R}_3, \vec{R}'_1$ (see Fig. 1 of Ref. 1) and at the other sites spin down, plus its complementary state. But there is another state, the $|\varphi_{\vec{k}}(\vec{R}_2, \vec{R}_3, \vec{R}'_1 k)\rangle$, which is degenerate to the states belonging to the \vec{k}_2 and \vec{k}_3 representations, with energy -16.202 mK which is very near to the doubly degenerate ground state. Its analytical form is

$$|\varphi_{\vec{k}}(\vec{R}_2, \vec{R}_3, \vec{R}'_1)\rangle = \frac{1}{\sqrt{2}}(S_0^+ S_{\vec{R}_2}^+ S_{\vec{R}_3}^+ S_{\vec{R}'_1}^+ |0\rangle - S_{\vec{R}_2}^+ S_{\vec{R}_3}^+ S_{\vec{R}'_1}^+ |0\rangle). \quad (8)$$

The ground state and the above-mentioned states having nearly the same energies permit us to assume that the CMN crystal at 0 K will almost fit the following physical picture. The ground state of the system is fivefold degenerate, with two of the states, $S_0^+ S_{\vec{R}_2}^+ S_{\vec{R}_3}^+ S_{\vec{R}'_1}^+ |0\rangle$ and $S_{\vec{R}_2}^+ S_{\vec{R}_3}^+ S_{\vec{R}'_1}^+ |0\rangle$, being purely antiferromagnetic. These states are mutually complementary.

The above-mentioned picture is in absolute agreement with the "semiclassical" result of the ground state, which suggests that the expectation value of the spins of the cluster has the same behavior as the

above-mentioned absolute antiferromagnetic states.

The fact and the near coincidence of the quantum-mechanical and "semiclassical" energy suggest that the classical theory of Niemeijer³ is very useful as a first approximation of the ground state of dipolar crystals.

The small difference between the doubly degenerate ground state and the triply degenerate $|\varphi_{\vec{k}}(\vec{R}_2, \vec{R}_3, \vec{R}_1)\rangle$ is possibly due to the accuracy of the measurements of the lattice constants of CMN, which have been carried out at a finite temperature (Zalkin *et al.*).² As has been noted in the preceding section, the expectation value of magnetization per cluster of the ground state and of the other eigenstates is equal to zero. This is in absolute agreement with the experimental results of Abeshouse *et al.*⁶ and Fisher *et al.*,⁵ and with the whole of theoretical results. It is in disagreement with the experiments of Mess *et al.*⁴

For the excited states we can only make a conjecture about their physical significance. In a planned future publication,¹⁵ where with a simple thermodynamic model we study the crystal at finite temperature by means of the excited state energies found here, we find a transition at a temperature of 1.85 mK, which is very close to experimentally found transition temperatures of 1.8 mK (Ref. 4) or 1.9 mK (Ref. 5). There is also a coincidence of the theoretical and experimental forms of specific heat as a function of temperature.⁵ These facts enable us

to suggest that the density of states, which was produced from the excited states presented in this paper, gives the main contribution for small energies relative to the transition temperature.

APPENDIX

Theorem 1. Suppose that we have a spin Hamiltonian H and the N -spin space S . Then the minimum of the functional $\langle \Psi | H | \Psi \rangle$ in S , under the condition $\langle \Psi | \Psi \rangle = 1$, is smaller or equal to the energy of the classical spin system.

Proof. Consider S' a subset of S . If the minimum in S' is assumed for a state $|\Psi'\rangle$, this state belongs to the space S as well since S' is a subset of S . But there may be states belonging to S but not to S' for which the functional $\langle \Psi | H | \Psi \rangle$ assumes smaller values. Therefore the minimum in S is smaller or equal to the minimum in S' . Consider now the set of states consisting of single products of N one-spin states. Obviously this is a subset S' of the space S of all N -spin states, as no linear combinations are included in the set S' , i.e., linear combinations of states in S' do not belong to S . Since all classical spin states can be realized by substituting the classical spins by the spin expectation values $\langle \Psi' | \hat{S}_i | \Psi' \rangle$ with $|\Psi'\rangle$ belonging to the set S' , then the minimum of H in S' which is equivalent to the classical minimum, is larger or equal to the quantum-mechanical minimum. Q.E.D.

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¹⁴See AIP document no. PRBMD-28-1544-26 for 26 pages of the tables of eigenvalues and eigenvectors of H_0 for CMN belonging to the various irreducible representations of the translation group (in all there are eight tables, one for each representation). Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is \$1.50 for a microfiche, or \$5.00 for a photocopy. Air-mail is additional. Make checks payable to the American Institute of Physics.

¹⁵S. Thanos (unpublished).