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MAGNETISM

Magnetoelectric Effect and Magnetic Dynamics in the Gd_2CuO_4 Antiferromagnet

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Abstract—The magnetoelectric effect and the magnetic dynamics in Gd_2CuO_4 have been studied using a phenomenological approach and group-theory methods. Vector order parameters are introduced based on four magnetic sublattices. Invariant products of the order parameters are determined, from which the thermodynamic potential density is constructed. Using the spin-wave representation, the calculations can be significantly simplified and the ground orientation magnetic state can be presumably determined. The magnetic dynamics is described by the Landau–Lifshitz equations, from which the antiferromagnetic resonance frequency and the dynamic susceptibilities, namely, magnetic, antiferromagnetic, magnetoelectric, and antiferroelectric susceptibilities are found. The frequency and the susceptibility are shown to be controlled by applied electric field.

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1. INTRODUCTION

The magnetic properties of R_2CuO_4 (R = Nd, Pr, Sm, Eu, Gd) compounds are of significant interest. First, it is due to the fact that the oxides become electron-type superconductors when they are doped with Ce and Th impurities [1]. In this case, the antiferromagnetism of the CuO_2 planes is assumed to play important role in appearance of the superconductivity [2]. The Gd_2CuO_4 compound occupies a specific place in this class of oxides. Its doping with Ce and Th impurities does not lead to the appearance of superconductivity. The reason why no superconducting transition occurs is still not completely understood [3]. Up to 1994, it was assumed that all above-listed oxides retain the tetragonal symmetry down to the lowest temperatures at which the studies were performed [4]. In addition, as for the Nd_2CuO_4 compound, the problem is not completely solved as to whether the magnetic ordering of copper ion spins is preceded by the structural phase transition from the symmetric phase with space group $I4/mmm$ to the phase with space group $P4_2/mnm$, or the $I4/mmm$ symmetry is retained, and the observed lattice distortions are due to magnetostriction deformations [5]. The neutron diffraction study of a Gd_2CuO_4 single crystal [6] showed the existence of superstructure nuclear reflections in the phase with space symmetry $I4/mmm$. Those authors associated the existence of these reflections with rotations of the oxygen ions O(1) around the copper ions. What this means is the Gd_2CuO_4 compound undergoes a structural phase transition to the orthorhombic phase with space group *Acam* (*Cmca* in the standard setting and *Cmce* in the new notation). The magnetic ordering of the Gd_2CuO_4 compound was studied in detail in [7]. Those authors established that there are three magnetic ordering temperatures: 6.5, 20, and 270 K. The first temperature relates to the rare-earth subsystem. It was shown in [7] that the antiferromagnetic ordering of the CuO_2 layers is accompanied by the formation of a weakly-ferromagnetic moment whose magnitude is proportional to temperature. This circumstance is thought to be important, since any weakly-ferromagnetic moment cannot exist in crystal symmetry $I4/mmm$ in R_2CuO_4 [7]. The neutron diffraction studies, the magnetic measurements, and the study of antiferromagnetic resonance in Gd_2CuO_4 single crystals were performed in [3, 4]. The experiments on neutron diffraction and antiferromagnetic resonance (AFMR) allowed those authors to make a conclusion about the magnetic structure and the ground state of this compound in the framework of assumption that the crystal has the tetragonal symmetry. According to [3, 4], Gd_2CuO_4 belongs to the class of easy-plane collinear antiferromagnets with insignificant anisotropy in the basal plane. An important result of [3, 4] is the detection of the magnetic scattering in this compound corresponding to wave vector $\mathbf{k} = 0$; the magnetic scattering demonstrates the existence of ferromagnetic gado-

linium layers in the **ab** plane of the tetragonal crystal. In this case, the layers are antiferromagnetically ordered along the [0, 0, 1] direction.

A further neutron diffraction study of Gd_2CuO_4 using polarized neutrons was carried out in [8]. When interpreting the experimental results, space group *Cmca* was replaced by two space groups *Acam* and *Bbcm* for two "twins" which can be formed from the tetragonal phase to conserve axis *c* of the unit tetragonal cell. The authors of [8] verified once again that the strong antiferromagnetic bond between copper ions in the 001 planes in combination with the anisotropy that is formed due to the structural distortions leads to the formation of weakly ferromagnetic CuO_2 layers. At temperatures from 275 to 18 K, the ferromagnetic moments of the layers are ordered in parallel to each other, forming the weakly ferromagnetic phase. The interlayer interaction of the CuO_2 planes is weak. As the temperature becomes below 18 K, the increasing polarization of Gd ions changes the interlayer interaction to the antiferromagnetic interaction, which brings about the formation of the antiferromagnetic structure without weak ferromagnetism at 16 K. In [8], using the form-factors and geometric constant, the magnetic moments of gadolinium and copper were estimated at this temperature in the field 0.5 T to be $0.47\mu_B$/Gd and $0.03\mu_B$/Cu, respectively. Below 7 K, the Gd sublattices are ordered, which is confirmed by fast increasing the reflection intensities. The authors of [8] conclude that the gadolinium and copper sublattices are ordered with the same wave vector. However, this conclusion does not agree with an analysis of the magnetic ordering in Gd_2CuO_4 performed in [9]. It is also assumed in [8] that the Gd ions in positions (0, 0, $\pm z$) are nonequivalent, and the magnetic moments at these ions are irregular in magnitude. According to remarks of the authors of [8], the above assumption has no direct experimental justification.

The magnetoelectric effect in the Gd_2CuO_4 compound was studied in [9].The possibility of existence of the magnetoelectric effect is thought to be related to the fact that the antiferromagnetic ordering of copper spins leads to doubling the crystal lattice, conserving the system symmetry with respect to space inversion. By contrast, the ferromagnetic planes of the rare-earth spins, being coupled antiferromagnetically, violate the symmetry with respect to space inversion but do not influence the translation symmetry. In [9], when analyzing the magnetoelectric effect, it was supposed that the compound belongs to the orthorhombic class *mm'm*. This magnetic class allows the existence of the magnetoelectric effect and is characterized by two independent components of the magnetoelectric tensor. However, the choice of the magnetic class is not justified in [9]. Further studies of the magnetoelectric effect in this compound were carried out in [10]. It was found that the two-sublattice model of the gadolinium subsystem and the thermodynamic potential for describing the magnetoelectric effect proposed in [9] are inadequate to describe the magnetoelectric bond of M_x component of the magnetization and E_y component of electric field observed experimentally. In this work, we study the magnetoelectric effect in Gd_2CuO_4, describe the magnetic dynamics of spins localized at the gadolinium ions and the influence of external electric fields on the dynamics based on the known experimental data with allowance for the space symmetry given by group *Cmce* in the framework of the four-sublattice model for rare-earth spins.

The magnetoelectric effect at temperatures lower than 7 K is analyzed taking into account only the Gd subsystem, since, as noted above, the magnetic moments localized at the gadolinium ions have higher magnitude as compared to the magnetic moments at copper ions.

2. THERMODYNAMIC POTENTIAL AND SYMMETRY

Because, at low temperatures, the wave vector **k** in Gd_2CuO_4 is a zero, the magnetic and crystallochemical Brave lattices coincide (an example of considering systems with $\mathbf{k} \neq 0$ is given in [11]). The magnetic Brave lattice consists of atomic magnetic moments obtained from the same moment in the unit magnetic cell by translation to integer periods. It is convenient to consider the magnetic properties with allowance for the crystal symmetry using the concept of magnetic sublattice. Generally, the number of sublattices is equal to the number of the magnetic moments in the magnetic unit cell.

Gadolinium occupies the multiple Wyckoff position 8*d*; in other words, the unit cell contains eight ions. Without a fundamental damage to the study the magnetic properties, we shall not use the centering translation as an symmetry element. Then, we can consider a primitive cell instead of the unit cell [12]. There are several main causes for us to do this: the behavior of the atomic magnetic moments under action of the centering translation is unknown (they can change their direction); and it is more convenient to deal with a smaller number of atoms.

The primitive cell of Gd_2CuO_4 contains four gadolinium atoms. Each *j*th atom exhibits a magnetic moment $\mathbf{m}_j$; because of this, taking into account the translation symmetry, they form four magnetic sublattices. We introduce the local sublattice magnetization $\mathbf{M}_\nu(\mathbf{r})$ in a point with the radius-vector **r**; the magnetization is the sum of all the magnetic moments of the νth sublattice in a physically small volume ΔV_r in the vicinity of the point **r**:

$$\mathbf{M}_\nu(\mathbf{r}) = \frac{1}{\Delta V_r}\sum_j \mathbf{m}_{\nu j}. \quad (1)$$

The volume ΔV_r must satisfy the condition $a^3 \ll \Delta V_r \ll \lambda^3$, where λ is a characteristic size of the distribution heterogeneities (spin-wave length, domain wall thickness); a is the interatomic distance. The left side of the inequality implies that the number of particles in the volume ΔV_r is quite great. Averaging of Eq. (1), taking into account the condition, makes it possible to use a continuous medium approximation in both the statics and the dynamics. The local macroscopic magnetization of the crystal will be determined by the sum of the magnetizations of four the sublattices

$$\mathbf{M} = \mathbf{M}_1 + \mathbf{M}_2 + \mathbf{M}_3 + \mathbf{M}_4. \quad (2)$$

Introduce three antiferromagnetism vectors for four the sublattices

$$\mathbf{L}_a = \mathbf{M}_1 + \mathbf{M}_2 - \mathbf{M}_3 - \mathbf{M}_4, \quad (3)$$

$$\mathbf{L}_b = \mathbf{M}_1 - \mathbf{M}_2 + \mathbf{M}_3 - \mathbf{M}_4, \quad (4)$$

$$\mathbf{L}_c = \mathbf{M}_1 - \mathbf{M}_2 - \mathbf{M}_3 + \mathbf{M}_4. \quad (5)$$

In the introduced four-sublattice model, $\mathbf{L}_a$, $\mathbf{L}_b$, and $\mathbf{L}_c$ are the vector parameters of the antiferromagnetic order, and $\mathbf{M}$ is the vector parameter of the ferromagnetic order which appears when external field are applied.

Under action of the space elements of the symmetry, an atom with coordinates $\mathbf{r}_i$ transfers to the place of another atom with coordinates $\mathbf{r}_j$ or remains in its place:

$$g_\nu \mathbf{r}_i = h_\nu \mathbf{r}_i + \mathbf{t}_h = \mathbf{r}_j + \mathbf{a}_k,$$

where g_ν is the symmetry element of the space group; h_ν is the symmetry element of the point group; $\mathbf{t}_h$ is the nontrivial translation vector; and $\mathbf{a}_k$ is the returning translation vector. We write the coordinates of four gadolinium atoms in the *Cmce* set:

$$\begin{aligned} &1-(x, 0, 0), \quad 2-(-x, 0, 0), \\ &3-(x, 1/2, 1/2), \quad 4-(-x, 1/2, 1/2). \end{aligned} \quad (6)$$

Alternatively acting on four the atoms by the symmetry elements of space group *Cmce*, we obtain the schemes of their mutual interchangings and thus determine in which manner the sublattices are interchanged. Information on the interchangings is given in Table 1, where the symmetry elements are denoted as well as in [13]. Now, we shall build the Table of transformations of $\mathbf{M}$, $\mathbf{L}_a$, $\mathbf{L}_b$, and $\mathbf{L}_c$. The components of the vector order parameters are transformed only by certain irreversible transformations (ITs) of group *Cmce* [14] (group *Cmce* contains only one-dimensional irreversible transformations). To distribute the components over corresponding ITs, we should know, in which manner they are changed during transformations which transfer the crystal lattice to itself. Such transformations of the symmetry act on the vector order parameter by two ways. On the one hand, the symmetry element g_ν acting on the vector produces its common rotations, reflections, and inversion. On the other hand, it can interchange atoms, thus-changing the direction of the magnetization of the sublattices. In this case, the direction of the vector order parameter can be changed to opposite or remain the same. In order to take into account such a twofold action, we introduce the concept of even and odd symmetry elements. Let the symmetry element g_ν which does not change the order parameter sign is called even element and the symmetry element changing the sign is called odd element. Denote the even and odd elements as $g_\nu(+)$ and $g_\nu(-)$, respectively. Any interchangings of the sublattices do not change the sign of the macroscopic magnetization $\mathbf{M}$ of the crystal, because it consists of the sum of the sublattice magnetizations; thus, all its elements are even.

Table 1. Permutation of the atoms

Number of atom i	Symmetry elements							
	g_1	g_2	g_3	g_4	g_{25}	g_{26}	g_{27}	g_{28}
1	1	2	4	3	4	3	1	2
2	2	1	3	4	3	4	2	1
3	3	4	2	1	2	1	3	4
4	4	3	1	2	1	2	4	3

As a result, the symmetry transformation can be reduced to the formula which shows the manner in which the components of a vector $\mathbf{A}$ are changed:

$$g_\nu(\pm)\mathbf{A} = \pm\delta(g_\nu)\begin{pmatrix} R_{xx}(g_\nu) & 0 & 0 \\ 0 & R_{yy}(g_\nu) & 0 \\ 0 & 0 & R_{zz}(g_\nu) \end{pmatrix}\begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix}, \quad (7)$$

where $\mathbf{A} = \mathbf{M}$, $\mathbf{L}_a$, $\mathbf{L}_b$, $\mathbf{L}_c$; $\delta(g_\nu)$ is the factor that is -1 when vector $\mathbf{A}$ is axial and is subjected to action of the elements containing the space inversion (i.e., elements starting from g_{25}); the factor is $+1$ in all other cases. The expression is prefixed with the plus sign when the element is even and the minus sign when the element is odd. The vector components are transformed by the rotation matrices $R(g_\nu)$ each of which corresponds to element g_ν. In our case, all the rotation matrices $R(g_\nu)$ are diagonal.

We use Eq. (7) to the magnetic field $\mathbf{H}$, the electric field $\mathbf{E}$, and the crystal electric polarization $\mathbf{P}$, which we initially consider in the continuous medium approximation, i.e., $\mathbf{A} = \mathbf{H}$, $\mathbf{E}$, $\mathbf{P}$. In this case, it should be taken into account that $\mathbf{P}$ and $\mathbf{E}$ are the polar vectors, unlike all other vectors under consideration. The vectors for which the concept of even and odd elements does not play a role, e.g., $\mathbf{M}$ and $\mathbf{H}$ or $\mathbf{P}$ and $\mathbf{E}$, are transformed similarly. The transformations of the components of $\mathbf{M}$, $\mathbf{L}_a$, $\mathbf{L}_b$, $\mathbf{L}_c$, $\mathbf{H}$, $\mathbf{E}$, and $\mathbf{P}$ obtained using Eq. (7) are listed in Table 2.

At the same time, Table 2 is the character table for space group *Cmce*, which make it possible to distribute

Table 2. Transformation of the basis functions for *Cmce*

Irreducible representation	Symmetry elements								Basis functions
	g_1	g_2	g_3	g_4	g_{25}	g_{26}	g_{27}	g_{28}	
$\tau_1(A_g)$	1	1	1	1	1	1	1	1	L_{ax}
$\tau_2(A_u)$	1	1	1	1	−1	−1	−1	−1	L_{bx}
$\tau_3(B_{3g})$	1	1	−1	−1	1	1	−1	−1	M_x, H_x
$\tau_4(B_{3u})$	1	1	−1	−1	−1	−1	1	1	L_{cx}, P_x, E_x
$\tau_5(B_{2g})$	1	−1	1	−1	1	−1	1	−1	M_y, L_{az}, H_y
$\tau_6(B_{2u})$	1	−1	1	−1	−1	1	−1	1	L_{bz}, L_{cy}, P_y, E_y
$\tau_7(B_{1g})$	1	−1	−1	1	1	−1	−1	1	M_z, L_{ay}, H_z
$\tau_8(B_{1u})$	1	−1	−1	1	−1	1	1	−1	L_{by}, L_{cz}, P_z, E_z

the components of the vectors, knowing their transformations, over corresponding ITs. In Table 2, IT is denoted as τ_ν, and, in the parentheses, the designations used in [15] are indicated. The value −1 corresponds to the change in the component sign; the value 1 corresponds to the case when the component did not change its sign. The components of the vector order parameters, electric polarization, and external fields distributed over IT are the basis function of this IT. Before we build the thermodynamic potential, it is necessary to find invariant combinations of the basis functions (invariants) relative to symmetry operations of the space group and time inversion. The product of basis functions will be an invariant if the product of corresponding irreducible representations contains the unit representation: $\tau_1 \in \tau_{\nu_1} \times \tau_{\nu_2} \times ... \times \tau_{\nu_n}$. Using Table 2, we can elucidate, which of the invariants satisfying to this condition can exist. The thermodynamic potential will only contain even degrees in order parameter, since it must be invariant relative to the time inversion. We shall restrict our consideration to the invariants whose degrees in order parameter is not higher than two. We can find the combinations which do not satisfy the group symmetry but become invariant when a factor consisting of any component of the vector **P** is added to the product. Such invariants are called magnetoelectric or antiferroelectric. They are responsible for the magnetoelectric and antiferroelectric effects, respectively, in the thermodynamic potential. All possible invariant products relative to the symmetry of the space group and time inversion operation are written in Table 3.

The thermodynamic potential density of our system can be schematically written as $\Phi = \Phi_M + \Phi_P + \Phi_{MP} + \Phi_{LP} - \mathbf{MH} - \mathbf{PE}$, where Φ_M is the energy density of the magnetic subsystem; Φ_P is the energy density of the electric subsystem; Φ_{MP} is the energy density of the magnetoelectric subsystem; Φ_{LP} is the energy density of the antiferroelectric subsystem; invariant **MH** describes the interaction energy of the magnetic subsystem with the external magnetic field (Zeeman energy); and invariant **PE** describes the interaction energy of the electric subsystem with the external electric field. If we shall write the expression for Φ in detail, substituting the found invariants to the expression, we obtain:

$$\begin{aligned}\Phi = {} & J_0\mathbf{M}^2 + J_1\mathbf{L}_a^2 + J_2\mathbf{L}_b^2 + J_3\mathbf{L}_c^2 + K_1M_x^2 + K_2M_y^2 \\ & + K_3M_z^2 + K_4L_{ax}^2 + K_5L_{ay}^2 + K_6L_{az}^2 + K_7L_{bx}^2 + K_8L_{by}^2 \\ & + K_9L_{bz}^2 + K_{10}L_{cx}^2 + K_{11}L_{cy}^2 + K_{12}L_{cz}^2 + D_1M_yL_{az} \\ & + D_2M_zL_{ay} + D_3L_{by}L_{cz} + D_4L_{bz}L_{cy} + \kappa_1^{-1}P_x^2 + \kappa_2^{-1}P_y^2 \\ & + \kappa_3^{-1}P_z^2 + \gamma_1L_{bx}M_xP_x + \gamma_2L_{bx}M_yP_y + \gamma_3L_{bx}M_zP_z \\ & + \gamma_4L_{by}M_xP_y + \gamma_5L_{cz}M_xP_y + \gamma_6L_{by}M_yP_x + \gamma_7L_{cz}M_yP_x \\ & + \gamma_8L_{bz}M_xP_z + \gamma_9L_{cy}M_xP_z + \gamma_{10}L_{bz}M_zP_x + \gamma_{11}L_{cy}M_zP_x \\ & + \gamma_{12}L_{cx}M_zP_y + \gamma_{13}L_{cx}M_yP_z + \zeta_1L_{ay}L_{bz}P_x + \zeta_2L_{ay}L_{cx}P_x \\ & + \zeta_3L_{ay}L_{cy}P_x + \zeta_4L_{az}L_{cz}P_x + \zeta_5L_{ay}L_{cx}P_y \\ & + \zeta_6L_{az}L_{bx}P_y + \zeta_7L_{ay}L_{bx}P_z + \zeta_8L_{az}L_{cx}P_z - \mathbf{MH} - \mathbf{PE},\end{aligned} \quad (8)$$

where J_0, J_1, J_2, J_3 are the exchange interaction constants; K_1, K_2, ..., K_{12}, D_1, D_2, D_3, D_4 are the magnetic anisotropy constants; κ_1, κ_2, κ_3 are the electric susceptibilities; γ_1, γ_2, ..., γ_{13} are the coefficients of the magnetoelectric interaction; and ζ_1, ζ_2, ..., ζ_8 are the coefficients of the antiferroelectric interaction. In the potential written, the terms with the coefficients γ_4 and γ_5 correspond to the dependence of M_x on E_y which was found experimentally and was not described by the two-sublattice model in [10]; this fact allows the conclusion that the approach chosen for describing the magnetoelectric effect is valid. The application of the obtained thermodynamic potential is hampered; however, we shall use, in what follows, the method of spin-wave representations [16] that make it possible to simplify the potential and the consideration of the problem as whole.

In the exchange approximation, Gd_2CuO_4 exhibits the collinear antiferromagnetic structure. It implies

Table 3. Invariant products of the basis functions

Product of the representations	Invariant combinations	
	magnetic	electric
$\tau_1 \times \tau_1$	L_{ax}^2	
$\tau_2 \times \tau_2$	L_{bx}^2	
$\tau_3 \times \tau_3$	M_x^2	
$\tau_4 \times \tau_4$	L_{cx}^2	P_x^2
$\tau_5 \times \tau_5$	$M_y^2,\ L_{az}^2,\ M_yL_{az}$	
$\tau_6 \times \tau_6$	$L_{bz}^2,\ L_{cy}^2,\ L_{bz}L_{cy}$	P_y^2
$\tau_7 \times \tau_7$	$M_z^2,\ L_{ay}^2,\ M_zL_{ay}$	
$\tau_8 \times \tau_8$	$L_{by}^2,\ L_{cz}^2,\ L_{by}L_{cz}$	P_z^2
	magnetoelectric	antiferroelectric
$\tau_2 \times \tau_3 \times \tau_4$	$L_{bx}M_xP_x$	
$\tau_2 \times \tau_5 \times \tau_6$	$L_{bx}M_yP_y$	$L_{az}L_{bx}P_y$
$\tau_2 \times \tau_7 \times \tau_8$	$L_{bx}M_zP_z$	$L_{ay}L_{bx}P_z$
$\tau_3 \times \tau_6 \times \tau_8$	$L_{by}M_xP_y,\ L_{bz}M_xP_z,\ L_{cy}M_xP_z,\ L_{cz}M_xP_y$	
$\tau_4 \times \tau_5 \times \tau_8$	$L_{by}M_yP_x,\ L_{cx}M_yP_z,\ L_{cz}M_yP_x$	$L_{az}L_{by}P_x,\ L_{az}L_{cx}P_z,\ L_{az}L_{cz}P_x$
$\tau_4 \times \tau_6 \times \tau_7$	$L_{bz}M_zP_x,\ L_{cx}M_zP_y,\ L_{cy}M_zP_x$	$L_{ay}L_{bz}P_x,\ L_{ay}L_{cx}P_y,\ L_{ay}L_{cy}P_x$

that the ionic magnetic moments can only be oriented parallel or antiparallel to any one direction. This direction also can have a certain orientation with respect to the crystallographic axes. In this case, various orientation states (phase) of the same exchange magnetic structure are considered. Which of possible orientation state for given structure forms under one or other conditions are determined by the magnetoanisotropic interactions of relativistic origin which is insignificant in Gd_2CuO_4 as compared to the exchange interaction. Owing to this fact, the orientation state can usually be changed by magnetic field, pressure, temperature, and (in our case) electric field too. Such transitions from one equilibrium orientation state to other are called orientational (or reorientational) magnetic phase transitions.

Every phase (or energy of the phase) must have own IT [15]. The spin-wave representation is the direct product of two irreducible representations of the phase. Since the ground state energy is a constant, the basis functions entering into IT of the phase are constant. For every spin-wave representation, there is a set of independent dynamic variables (spin-wave modes). The dynamic variables are the time-dependent basis functions which are transformed by the representations determining given spin-wave representation. All the basis functions, exception for the dynamic variables and functions of the ground orientational state are zeros. The study of the magnetic dynamics is simplified by using the approach based on finding spin-wave representations for the phase under consideration. For example, the dynamic variables can be found even before writing the equations of motion, and it allows us to write the independent system of the Landau–Lifshitz equation for every set. We shall restrict ourselves to consideration of only the terms in the potential in which the product of the dynamic variables give the degree not higher than two.

Let us choose the phase $\tau_6(\overline{L}_{bz},\ \overline{L}_{cy})$, where $\overline{L}_{bz}$ and $\overline{L}_{cy}$ are the ground magnetic orientational states (the bar above the letter indicates that L is constant). The symmetry allows the existence of the $\overline{L}_{bz}$ and $\overline{L}_{cy}$ states with equal possibility. In a real system, one of the components is significantly larger than another. Which of them is larger can only be known from the microscopic theory or experiment. It is beyond the phenomenological theory, but two the quantities can be considered together, taking into account that weak relativistic interactions giving a small noncollinearity can exist; in this case, in the exchange approximation, the antiferromagnet will continue be collinear.

IT of the phase can be obtained using the direct product of IT of the $\tau_3(M_x)$ phase and IT of the $\tau_8(L_{by}, L_{cz})$: $\tau_6(\overline{L}_{bz}, \overline{L}_{cy}) = \tau_3(M_x) \times \tau_8(L_{by}, L_{cz})$. In other words, $\tau_{38}(M_x, L_{by}, L_{cz})$ is the mode, where M_x, L_{by}, and L_{cz} are the dynamic variables dependent on time t. A main reason of choosing phase τ_6 and corresponding mode τ_{38} is that they retain in potential necessary magnetoelectric terms which were found experimentally, namely: $M_x(E_y)$ and $M_x(E_z)$. In other phases, the experimental dependences present incompletely or give higher orders than it is required. Note that fields E_y, E_z, H_x will not change the ground state from the symmetry standpoint, because they are transformed by ITs of the phase and the mode.

For phase $\tau_6(\overline{L}_{bz}, \overline{L}_{cy})$, the number of the terms entering into the full thermodynamic potential decreases significantly. With the inclusion of spin-wave mode $\tau_{38}(M_x, L_{by}, L_{cz})$, the thermodynamic potential density (the energy of the ground magnetic state) can be rewritten as follows:

$$\begin{aligned}\Phi = \Phi_0(\overline{L}_{bz}^2, \overline{L}_{cy}^2, \overline{L}_{bz}\overline{L}_{cy}) + (J_0 + K_1)M_x^2 \\ + (J_2 + K_8)L_{by}^2 + (J_3 + K_{12})L_{cz}^2 + D_3 L_{by}L_{cz} + \kappa_1^{-1}P_x^2 \\ + \kappa_2^{-1}P_y^2 + \kappa_3^{-1}P_z^2 + \gamma_4 L_{by}M_xP_y + \gamma_5 L_{cz}M_xP_y \\ + \gamma_8\overline{L}_{bz}M_xP_z + \gamma_9\overline{L}_{cy}M_xP_z - M_xH_x \\ - P_xE_x - P_yE_y - P_zE_z,\end{aligned} \tag{9}$$

where $\Phi_0(\overline{L}_{bz}^2, \overline{L}_{cy}^2, \overline{L}_{bz}\overline{L}_{cy})$ is the constant consisting of the invariants which do not depend on the dynamic variables.

We use the equilibrium conditions for the thermodynamic potential: $\partial\Phi/\partial P_x = 0$, $\partial\Phi/\partial P_y = 0$, $\partial\Phi/\partial P_z = 0$. Minimizing the potential with respect to P_x, P_y, P_z, we obtain the system of equations, from which we can separate the dependences of P_x, P_y, P_z on the dynamic variables of mode $\tau_{38}(M_x, L_{by}, L_{cz})$:

$$\begin{cases} P_x = \frac{1}{2}\kappa_1 E_x \\ P_y = \frac{1}{2}\kappa_2 E_y - \frac{1}{2}\kappa_2\gamma_4 L_{by}M_x - \frac{1}{2}\kappa_2\gamma_5 L_{cz}M_x \\ P_z = -\frac{1}{2}\kappa_3 E_z - \frac{1}{2}\kappa_3\gamma_8 L_{bz}M_x - \frac{1}{2}\kappa_3\gamma_9 L_{cy}M_x. \end{cases} \tag{10}$$

The application of these conditions is allowable, because we assume, for simplicity, that polarization **P** has time to be changed quite fast in the wake of changes in the dynamic variables.

There is one more possibility to simplify the calculations, considering an equally modulus model, in which the magnetic moment lengths are equal to each other and are unchanged:

$$\mathbf{M}_1^2 = \mathbf{M}_2^2 = \mathbf{M}_3^2 = \mathbf{M}_4^2 = M_0^2 = \text{const}. \tag{11}$$

where M_0 is the magnetization magnitude of a sublattice. From this conditions, the expressions follow relating the order parameters to each other; namely, we obtain three systems of equations for the four-sublattice model:

$$\begin{cases} \mathbf{M}\mathbf{L}_a + \mathbf{L}_b\mathbf{L}_c = 0 \\ \mathbf{M}\mathbf{L}_b + \mathbf{L}_a\mathbf{L}_c = 0 \\ \mathbf{M}\mathbf{L}_c + \mathbf{L}_a\mathbf{L}_b = 0. \end{cases} \tag{12}$$

Taking into account that we consider phase $\tau_6(\overline{L}_{bz}, \overline{L}_{cy})$ and mode $\tau_{38}(M_x, L_{by}, L_{cz})$, we obtain, from conditions (12), the relationship $L_{cz} = -\overline{L}_{cy}\overline{L}_{bz}^{-1}L_{by}$, owing to which only two dynamic variables are retained in the problem under consideration. Substituting all obtained relationships into the thermodynamic potential, we write it in the final form:

$$\begin{aligned}\Phi = \frac{\kappa_3}{4}(4\kappa_3^{-1}J_0 - \gamma_8^2\overline{L}_{bz}^2 - \gamma_9^2\overline{L}_{cy}^2 - 3\gamma_8\gamma_9\overline{L}_{bz}\overline{L}_{cy})M_x^2 \\ + \left(J_2 + K_8 + (J_3 + K_{12})\frac{\overline{L}_{cy}^2}{\overline{L}_{bz}^2} - D_3\frac{\overline{L}_{cy}}{\overline{L}_{bz}}\right)L_{by}^2 \\ + \frac{3\kappa_2}{4}\left(\gamma_4 - \gamma_5\frac{\overline{L}_{cy}}{\overline{L}_{bz}}\right)E_yL_{by}M_x \\ + \left(\frac{3\kappa_3}{4}(\gamma_8\overline{L}_{bz} + \gamma_9\overline{L}_{cy})E_z - H_x\right)M_x \\ - \frac{1}{4}(\kappa_1E_x^2 + \kappa_2E_y^2 + \kappa_3E_z^2).\end{aligned} \tag{13}$$

3. AFMR AND DYNAMIC SUSCEPTIBILITIES

The dynamics of vector order parameters **M**, $\mathbf{L}_a$, $\mathbf{L}_b$, $\mathbf{L}_c$ is described using the Landau–Lifshitz equations formulated for the four-sublattice model:

$$\begin{aligned}\frac{1}{\gamma}\dot{\mathbf{M}} &= \left[\mathbf{M}, \frac{\partial\Phi}{\partial\mathbf{M}}\right] + \left[\mathbf{L}_a, \frac{\partial\Phi}{\partial\mathbf{L}_a}\right] + \left[\mathbf{L}_b, \frac{\partial\Phi}{\mathbf{L}_b}\right] + \left[\mathbf{L}_c, \frac{\partial\Phi}{\partial\mathbf{L}_c}\right], \\ \frac{1}{\gamma}\dot{\mathbf{L}}_a &= \left[\mathbf{M}, \frac{\partial\Phi}{\partial\mathbf{L}_a}\right] + \left[\mathbf{L}_a, \frac{\partial\Phi}{\partial\mathbf{M}}\right] + \left[\mathbf{L}_b, \frac{\partial\Phi}{\mathbf{L}_c}\right] + \left[\mathbf{L}_c, \frac{\partial\Phi}{\partial\mathbf{L}_b}\right], \\ \frac{1}{\gamma}\dot{\mathbf{L}}_b &= \left[\mathbf{M}, \frac{\partial\Phi}{\partial\mathbf{L}_b}\right] + \left[\mathbf{L}_a, \frac{\partial\Phi}{\partial\mathbf{L}_c}\right] + \left[\mathbf{L}_b, \frac{\partial\Phi}{\mathbf{M}}\right] + \left[\mathbf{L}_c, \frac{\partial\Phi}{\partial\mathbf{L}_a}\right], \\ \frac{1}{\gamma}\dot{\mathbf{L}}_c &= \left[\mathbf{M}, \frac{\partial\Phi}{\partial\mathbf{L}_c}\right] + \left[\mathbf{L}_a, \frac{\partial\Phi}{\partial\mathbf{L}_b}\right] + \left[\mathbf{L}_b, \frac{\partial\Phi}{\mathbf{L}_a}\right] + \left[\mathbf{L}_c, \frac{\partial\Phi}{\partial\mathbf{M}}\right],\end{aligned} \tag{14}$$

where γ is the scalar magnetomechanical ratio. From the 12 Landau–Lifshitz equations for phase $\tau_6(\overline{L}_{bz}$,

$\bar{L}_{cy}$) under study and spin-wave mode $\tau_{38}(M_x, L_{by}, L_{cz})$, we immediately obtain the independent system of equations for two dynamic variables:

$$\begin{cases} \dot{M}_x = -\gamma \bar{L}_{bz} \dfrac{\partial \Phi}{\partial L_{by}} \\ \dot{L}_{by} = \gamma \bar{L}_{bz} \dfrac{\partial \Phi}{\partial M_x}. \end{cases} \quad (15)$$

We apply to the crystal fields E_y = const, $E_z(t) = E_z^0 \exp(-i\omega t)$, and $H_x(t) = H_x^0 \exp(-i\omega t)$, where ω is the frequency of the external fields which, as noted above, do not change the ground orientational state. Then, substituting the thermodynamic potential density in Eq. (15), we obtain

$$\begin{cases} \dot{M}_x = 2\gamma \bar{L}_{bz}(D_3 \bar{L}_{bz} \bar{L}_{cy} - (J_2 + K_8)\bar{L}_{bz}^2 \\ -(J_3 + K_{12})\bar{L}_{cy}^2) L_{by} - \dfrac{3\gamma\kappa_2}{4}(\gamma_5 \bar{L}_{cy} - \gamma_4 \bar{L}_{bz}) E_y M_x, \\ \dot{L}_{by} = -\dfrac{2\gamma\kappa_3 \bar{L}_{bz}}{4}(\gamma_8^2 \bar{L}_{bz}^2 + \gamma_9^2 \bar{L}_{cy}^2 + 3\gamma_8\gamma_9 \bar{L}_{bz}\bar{L}_{cy} \\ -4\kappa_3^{-1} J_0) M_x + \dfrac{3\gamma\kappa_2}{4}(\gamma_5 \bar{L}_{cy} - \gamma_4 \bar{L}_{bz}) E_y L_{by} \\ + \dfrac{3\gamma\kappa_3 \bar{L}_{bz}}{4}(\gamma_8 \bar{L}_{bz} - \gamma_9 \bar{L}_{cy}) E_z - \gamma \bar{L}_{bz} H_x. \end{cases} \quad (16)$$

The solution of this simple system of equations at zero fields are $M_x(t) = M_x^0 \exp(-i\Omega_0 t)$ and $L_{by}(t) = L_{by}^0 \exp(-i\Omega_0 t)$, where M_x^0 and L_{by}^0 are the amplitudes of the dynamic variable vibrations. We equalize the terms with coefficients γ_8 and γ_9 to zero, because there is no magnetoelectric effect in the absence of external electric field and spontaneous polarization. From the system, we find the AFMR eigenfrequency

$$\Omega_0^2 = 4\gamma^2 J_0((J_2 + K_8)\bar{L}_{bz}^2 + (J_3 + K_{12})\bar{L}_{cy}^2 - D_3 \bar{L}_{bz}\bar{L}_{cy}). \quad (17)$$

When applying electric field E_y = const, the AFMR eigenfrequency increases by the term dependent on this field

$$\Omega_E^2 = \left(\frac{3\gamma\kappa_2}{4}(\gamma_4 \bar{L}_{bz} - \gamma_5 \bar{L}_{cy})\right)^2 E_y^2. \quad (18)$$

Now, to find the dynamic susceptibilities, we express M_x from the system of equations (16) in terms of external fields E_z and H_x and obtain

$$M_x^0 = \frac{3\kappa_3 L(\gamma_8 \bar{L}_{bz} + \gamma_9 \bar{L}_{cy})}{2(\omega_0^2 - \omega^2)} E_z^0 - \frac{2L}{\omega_0^2 - \omega^2} H_x^0, \quad (19)$$

where

$$L = \gamma^2(D_3 \bar{L}_{bz}\bar{L}_{cy} - (J_2 + K_8)\bar{L}_{bz}^2 - (J_3 + K_{12})\bar{L}_{cy}^2), \quad (20)$$

and $\omega_0^2 = \Omega_0^2 + \Omega_E^2$ is the frequency of vibrations of the dynamic variables (at fields E_z and H_x, we should include to Ω_0 terms with γ_8 and γ_9). The dependence of the magnetization on the external magnetic field and external electric field is expressed by relationship $M_i = \alpha_{ij} E_j + \chi_{ij} H_j$, and, with inclusion of the chosen fields, this relationship can be rewritten as $M_x = \alpha_{xz} E_z + \chi_{xx} H_x$. Comparing this dependence with the expression for the magnetization, we can find the dynamic magnetoelectric susceptibility α_{xz}

$$\alpha_{xz} = \frac{3\kappa_3 L(\gamma_8 \bar{L}_{bz} + \gamma_9 \bar{L}_{cy})}{2(\omega_0^2 - \omega^2)} \quad (21)$$

and the dynamic magnetic susceptibility χ_{xx}

$$\chi_{xx} = -\frac{2L}{\omega_0^2 - \omega^2}. \quad (22)$$

Proceeding in the same manner as in the case of M_x, we express L_{by} in terms of the external field. Then, we obtain that $L_{by} = \beta_{yz}^{(L_b)} E_z^0 + \delta_{yx}^{(L_b)} H_x^0$, where β_{yz} is the dynamic antiferroelectric susceptibility, and δ_{yx} is the dynamic antiferromagnetic susceptibility. For two the latter quantities, we have the expressions as follows:

$$\beta_{yz} = -i\omega \frac{3\gamma\kappa_3 \bar{L}_{bz}(\gamma_8 \bar{L}_{bz} + \gamma_9 \bar{L}_{cy})}{4\omega_0^2 - \omega^2}, \quad (23)$$

$$\delta_{yx} = i\omega \frac{\gamma \bar{L}_{bz}}{\omega_0^2 - \omega^2}. \quad (24)$$

4. CONCLUSIONS

In this work, we have demonstrated the application of group-theoretical methods using, as an example, the four-sublattice model for the gadolinium subsystem in Gd_2CuO_4. The group-theoretical analysis of the potential shows that it contains the terms of the magnetoelectric interactions corresponding to the dependences of M_x on E_y and M_x on E_z found in the experiment. The inclusion of the evenness of elements $g_v(\pm)$ makes it possible to distribute the basis functions over irreducible representations for space group *Cmce*. The latter in combination with the experimental data on the magnetoelectric effect allow the assumption on the orientational state of magnetic sublattices at low temperatures, namely: we proposed phase $\tau_6(\bar{L}_{bz}, \bar{L}_{cy})$ and spin-wave mode $\tau_{38}(M_x, L_{by}, L_{cz})$. Using Table 2, it is possible to suppose which external fields can change the orientational state in the crystal; for example, field E_x can change the state to L_{cx}, field H_y can change the state to L_{az}, and field H_z can change the state to L_{ay}.

The theory of spin-wave representations allowed us to find the dynamic quantities and obtain the system of

the Landau–Lifshitz equations for them, and also to substantially decrease the number of terms in the thermodynamic potential. From the system of equations, we found the eigenfrequency of the antiferromagnetic resonance Ω_0. The inclusion of the magnetoelectric interactions allowed us to tell about the existence of the eigenfrequency shift by external electric field E_y.

We calculated the dynamic susceptibilities α_{xz}, χ_{xx}, β_{yz}, and δ_{yx} which have a resonance character, and the resonance can be controlled by external field E_y. Alternative calculations of the dynamic susceptibilities are very complex, they need a complex mathematics and numerical methods. The antiferroelectric and antiferromagnetic susceptibilities make it possible to take into account the heat loss related to the excitation of antimagnons by external fields. To obtain other tensor components of the dynamic susceptibilities, the orientational state should be changed (e.g., we should apply external field which do not enter to phase $\tau_6(\overline{L}_{bz}, \overline{L}_{cy})$ and mode $\tau_{38}(M_x, L_{by}, L_{cz})$. For other orientational state, we should consider new phases and spin-wave modes, for which the thermodynamic potential and the Landau–Lifshitz equations will be other. It should be noted that the magnetic-dynamics equation did not include the relaxation; alternatively, the description of the magnetodynamics becomes more complex problem, and the conditions of the equally-modulus model cease to be fulfilled [16]. The inclusion of the relaxation would make it impossible to use of group-theoretical methods in this simple application. This approach is one of a few which make it possible to build the thermodynamic potential and then to analyze it. In addition, we note that the approach presented in this work can be used to consider and predict many effects, e.g., to predict the photogalvanic effect in a centroantisymmetric antiferromagnet [17].

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REFERENCES

1. Y. Tokura, H. Takagi, and S. Uchida, Nature (London) **337**, 345 (1989).
2. M. Yu. Izyumov, Sov. Phys.—Usp. **34** (11), 935 (1991).
3. T. Chattopadhyay, P. J. Brown, A. A. Stepanov, P. Wyder, J. Voiron, A. I. Zvyagin, S. N. Barilo, D. I. Zhigunov, and I. Zobkalo, Phys. Rev. B: Condens. Matter **44**, 9486 (1991).
4. T. Chattopadhyay, P. J. Brown, B. Roessli, A. A. Stepanov, S. N. Barilo, and D. I. Zhigunov, Phys. Rev. B: Condens. Matter **46**, 5731 (1992).
5. A. A. Stepanov, P. Wyder, T. Chattopadhyay, P. J. Brown, G. Fillion, I. M. Vitebsky, A. Deville, B. Gaillard, S. N. Barilo, and D. I. Zhigunov, Phys. Rev. B: Condens. Matter **48**, 12979 (1993).
6. M. Braden, W. Paulus, A. Cousson, P. Vigoureux, G. Heger, A. Goukassov, P. Bourges, and D. Petitgrand, Europhys. Lett. **25** (8), 625 (1994).
7. J. D. Thompson, S. W. Cheong, S. E. Brown, Z. Fisk, S. B. Oseroff, M. Tovar, D. C. Vier, and S. Schults, Phys. Rev. B: Condens. Matter **39**, 6660 (1989).
8. P. J. Brown and T. Chatterji, arXiv:1105.6196v1 (2011).
9. H. Wiegelmann, A. A. Stepanov, I. M. Vitebsky, A. G. M. Jansen, and P. Wyder, Phys. Rev. B: Condens. Matter **49**, 10039 (1994).
10. A. I. Smirnov and I. N. Kilyustikov, JETP **81** (2), 384 (1995).
11. V. V. Men'shenin, Phys. Solid State **54** (10), 2015 (2012).
12. E. A. Turov, A. V. Kolchanov, V. V. Men'shenin, I. F. Mirsaev, and V. V. Nikolaev, *Symmetry and Physical Properties of Antiferromagnets* (Nauka, Moscow, 2001) [in Russian].
13. O. V. Kovalev, *Irreducible and Induced Representations and Co-Representations of Fedorov's Groups* (Nauka, Moscow, 1986) [in Russian].
14. E. A. Turov and V. V. Nikolaev, Phys.—Usp. **48** (5), 431 (2005).
15. L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics*, Vol. 3: *Quantum Mechanics: Non-Relativistic Theory* (Fizmatlit, Moscow, 2004; Butterworth–Heinemann, Oxford, 2005).
16. E. A. Turov, A. V. Kolchanov, V. V. Men'shenin, I. F. Mirsaev, and V. V. Nikolaev, Phys.—Usp. **41** (12), 1191 (1998).
17. V. V. Men'shenin, Phys. Solid State **46** (11), 2081 (2004).

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