Magnetic-ordering-induced one-phonon infrared absorption in Nd_2CuO_4

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The effect of magnetic ordering accompanied by multiplication of the unit cell of the crystal and by folding of the Brillouin zone on the one-phonon infrared absorption spectrum is investigated. One-phonon absorption by phonons from the Brillouin-zone boundary of the paramagnetic phase of Nd_2CuO_4, which is described by the $I4/mmm$ space group, is discovered for the first time in the magnetically ordered phase of this crystal. The spin-dependent electric-dipole and magnetic-dipole mechanisms of absorption from the M and X points on the Brillouin-zone boundary of the paramagnetic phase are considered. A criterion for the appearance of the one-phonon electric-dipole mechanism of absorption from the Brillouin-zone boundary upon a magnetic phase transition with multiplication of the unit cell is formulated. Measurements performed in a magnetic field exceeding the spin-reorientation phase transition field demonstrate its influence on some absorption lines and permit their identification with Brillouin-zone boundary phonons. The measurements performed confirm the presence of a crosslike exchange-noncollinear magnetic structure in Nd_2CuO_4, and it is concluded that there are no structural distortions in the temperature range 150–300 K. © *1996 American Institute of Physics.* [S1063-7761(96)02704-7]

1. INTRODUCTION

When a magnetic phase transition accompanied by n-fold multiplication of the original unit cell takes place, the magnetic Brillouin zone becomes n times smaller than the Brillouin zone of the original paramagnetic phase. The lowering of the translational symmetry associated with such a phase transitions is described by the magnetic order parameter, which has the symmetry of one of the high-symmetry points or Lifshitz points on the Brillouin-zone boundary of the paramagnetic phase. Therefore, the states of quasiparticles which previously belonged to these and some other points on the Brillouin-zone boundary turn out to be at the Brillouin-zone center of the magnetically ordered phase. Some of these states become accessible to observation by one-particle Raman scattering spectroscopy and optical absorption spectroscopy. The mechanisms for the absorption and scattering of light by these quasiparticles appear after magnetic ordering and are specified by the symmetry and the absolute value of the magnetic order parameter. Such spin-dependent mechanisms should be sensitive to changes in the ground state of the magnetic subsystem and to the effects of a magnetic field which causes reorganization of the magnetic structure. As a rule, the variation of the energy of the quasiparticles displayed in the scattering and absorption spectra after a magnetic phase transition can be neglected in view of the weakness of their interactions with the magnetic subsystem compared with the energies of the quasiparticles themselves.

The phenomenon of magnetic-ordering-induced one-phonon Raman scattering on boundary phonons with multiplication of the original crystallographic cell has been discovered in several magnetic semiconductors. The work in this area has been reviewed in Ref. 1. However, one-phonon absorption caused by folding of the Brillouin zone is not observed in these systems, despite the efforts undertaken specially to detect it.[2] As follows from the results presented in Ref. 1, the microscopic mechanisms which allow scattering on phonons belonging to the Brillouin-zone boundary of a paramagnetic phase are fairly complicated, vary from object to object, and, in the final analysis, are caused by the selective action of the optical phonons on the electronic subsystem and the subsystem of localized spins. Therefore, a more constructive approach would be to formulate phenomenological symmetry conditions for the possibility of observing this phenomenon on the basis of the symmetry group of the paramagnetic phase. Here it is understood that the phase transition to the magnetically ordered state is a second-order phase transition; therefore, the symmetry group of the magnetically ordered phase is a subgroup of the symmetry group of the paramagnetic phase.

Our study has shown that the type of magnetic ordering imposes restrictions on the existence of an electric-dipole

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absorption mechanism. In particular, after a magnetic phase transition with doubling of the unit cell, the one-phonon electric-dipole absorption mechanism on Brillouin-zone boundary phonons does not operate. Such restrictions do not exist in the case of Raman scattering. This is apparently the reason why spin-dependent one-phonon absorption was not observed in a VI_2 crystal, while spin-dependent one-phonon scattering was observed.[2]

The symmetry analysis which we performed showed that one-particle electric-dipole absorption by boundary phonons is possible only if the magnetic ordering is described by a multicomponent or at least a two-component order parameter, each of whose components has different translational symmetry (for example, belongs to different rays of a Lifshitz point of the Brillouin zone of the paramagnetic phase). A one-phonon magnetic-dipole absorption mechanism, which is weaker in intensity, occurs for all types of magnetic ordering. If the ground-state symmetry of the magnetic subsystem permits the existence of both mechanisms, each of them allows absorption by states of phonons belonging to different points on the Brillouin-zone boundary of the paramagnetic phase. The latter is due to the different parities of these mechanisms with respect to the time-reversal operation.

The compound Nd_2CuO_4 is one of the crystalline substances in which a magnetic structure allowing one-phonon electric-dipole absorption by boundary phonons can occur. It has a crosslike four-sublattice magnetic exchange-noncollinear structure,[3–7] which, however, can appear in two ways. In one case it is postulated that magnetic ordering occurs at $T_N=276$ K with quadrupling of the original unit cell of the paramagnetic phase, which is described by the $I4/mmm$ space group,[4,5] and in the other case it is assumed that cross-like magnetic ordering occurs without multiplication of the unit cell after a postulated structural phase transition at 300 K, which precedes the magnetic ordering.[3] The paramagnetic phase appearing after the structural phase transition is described by the $P4_2/mnm$ group.[8] The unit cell of this phase is a quadrupled, structurally distorted form of the cell of the $I4/mmm$ phase.[8] Structural distortions like those investigated in Ref. 8 should be caused by displacements of the copper, neodymium, and intralayer oxygen.

In both cases the Brillouin zone observed below the Néel temperature is four times smaller than the Brillouin zone of the $I4/mmm$ phase. The folding of the Brillouin zone, both as a result of magnetic ordering directly from the $I4/mmm$ phase and as a result of the $I4/mmm \rightarrow P4_2/mnm$ structural phase transition, increases the number of phonons which should be observed for $\mathbf{k}=0$ (Ref. 9).

One fundamental difference between these two possible ways to achieve magnetic ordering is that in the first case the mechanisms which permit absorption by certain boundary phonons in the $I4/mmm$ phase are spin-dependent and, therefore, sensitive to the effects of a magnetic field. In the second case the intensity of the absorption by such phonons is determined by the magnitude of the structural distortions and is, therefore, not dependent on the strength of the external magnetic field. Investigating the absorption spectra in a magnetic field makes it possible to determine just which case is actually realized. The available published data from studies of the phonon spectra of Nd_2CuO_4 using inelastic neutron scattering,[10] infrared (IR) absorption,[11] and Raman scattering spectroscopy[11–14] in the absence of an external magnetic field are, in principle, insufficient for unequivocally answering questions regarding the existence of structural distortions.

The investigations which we performed demonstrated the presence of lines whose intensity depends on the magnetic field in the infrared region of the reflectance spectrum of Nd_2CuO_4. It is important to stress that the positions of these lines correspond to the frequencies of boundary phonons of the $I4/mmm$ phase determined by inelastic neutron scattering spectroscopy.[10] Thus, the influence of a magnetic phase transition with multiplication of the unit cell and folding of the Brillouin zone on the one-phonon absorption spectra of magnets has been discovered for the first time. This phenomenon indicates that no structural phase transition occurs in Nd_2CuO_4 at $T=300$ K or in the temperature range down to 150 K, at which the experiments were performed.

2. INFLUENCE OF THE STRUCTURAL PHASE TRANSITION ON THE TRANSFORMATION OF THE PHONON SPECTRUM OF Nd_2CuO_4

Above $T=300$ K crystalline Nd_2CuO_4 belongs to the $I4/mmm$ (D_{4h}^{17}) symmetry group. The unit cell contains one formula unit, and there are, therefore, 21 vibrational degrees of freedom, which form the mechanical representation d_m. For $\mathbf{k}=0$ these degrees of freedom are distributed in the following manner among the irreducible representations of the D_{4h} point group:

$$d_m=A_{1g}+4A_{2u}+B_{1g}+B_{2u}+2E_g+5E_u. \tag{1}$$

The $I4/mmm$ group and the relation (1) make up the basis for interpreting the experimental results in Refs. 10–14. Nevertheless, some data in Refs. 11, 12, and 14, as discussed by the respective authors, do not fit the classification (1). For example, a number of lines of E_u phonons greater than the number following from (1) was observed in the IR absorption spectra in Ref. 11. They include, in particular, the weak lines at 165 cm^{-1} and 320 cm^{-1} shown in Fig. 3(b) in Ref. 11. The observation of a line in the Raman spectra at 590 cm^{-1}, which corresponds in energy to the E_u(LO) phonon, was also mentioned in that paper. We recall that in crystals having an inversion center it is impossible to observe phonons of such symmetry simultaneously in the scattering and absorption spectra (the alternative prohibition rule). Therefore, Crawford *et al.*[11] postulated an impurity mechanism for allowing light scattering. Other data which attracted our attention were given in Ref. 14, in which Raman scattering spectroscopy was used to investigate transitions between the components of the $^4I_{9/2}$ and $^4I_{11/2}$ multiplets of the Nd^{3+} ion, which are split by the crystal field. Jandl *et al.*[14] discovered that most of the peaks observed have a doublet structure with splitting of the order of 5 cm^{-1}, which remains practically unchanged in the temperature range 10–150 K. The presence of this splitting is inconsistent with the fairly high site symmetry of the Nd^{3+} ion indicated by the $I4/mmm$ group. Therefore, a Davydov type of scattering was postulated as an explanation in Ref. 14.

Let us consider the phenomena observed, assuming that a structural phase transition takes place at $T_C = 300$ K. Besides the data in Ref. 3, there are indications of the possibility of this transition in Ref. 10, in which inelastic neutron scattering by phonons in Nd_2CuO_4 at room temperature was investigated, and a tendency for suppression of the lowest-energy phonon mode at the X point of the Brillouin zone with decreasing temperature was noted. A thorough group-theoretical investigation of the structural transition in Nd_2CuO_4 was carried out in Ref. 8. We shall utilize the results of that work to examine the transformation of the phonon absorption and scattering spectra after the transition.

According to Ref. 8, the structural distortions appearing after the transition in Nd_2CuO_4 transform according to the two-dimensional irreducible representation τ_4 of the Lifshitz point of the Brillouin zone described by the two-ray star $K13$ with the rays

$$\mathbf{k}_1 = \frac{1}{2}\mathbf{b}_3 = \left(\frac{\pi}{2\tau}, \frac{\pi}{2\tau}, 0\right), \quad \mathbf{k}_2 = \frac{1}{2}(\mathbf{b}_1 - \mathbf{b}_2) = \left(-\frac{\pi}{2\tau}, \frac{\pi}{2\tau}, 0\right), \tag{2}$$

where the $\mathbf{b}_i$ are vectors of the reciprocal lattice (here and in the following we shall use the notations adopted in Ref. 15). As a result of the displacements, in which all the ions, except the oxygen ions in the CuO layers, participate, the translational symmetry is lowered, and the unsymmetrical phase is described by the $P4_2/mnm$ (D_{4h}^{14}) space group. The unit cell of this phase contains four formula units of Nd_2CuO_4. For $\mathbf{k} = 0$ the 85 vibrational degrees of freedom are distributed in the following manner among the irreducible representations of the D_{4h} group:[9]

$$\tilde{d}_m = 4A_{1g} + 2A_{2g} + 3A_{1u} + 8A_{2u} + 3B_{1g} + 5B_{2g} + 7B_{1u} + 2B_{2u} + 8E_g + 17E_u. \tag{3}$$

The site symmetry of the ions in the new phase was also given in Ref. 9.

One consequence of the lowering of the translational symmetry is the folding of the Brillouin zone. Because of the symmetry of the order parameter, additional phonon branches appear at the Brillouin-zone center of the new phase from the points on the Brillouin-zone boundary of the old phase $X = (1/2, 1/2, 0)$ and $M = (1, 0, 0)$ or the equivalent point $Z = (0, 0, 1)$. Since the displacements are small, and the energies of the phonons far from the transition point depend weakly on the temperature, all the lines following from (3) which are additional to (1) will have, first, a weak intensity and, second, energies corresponding to energies of the Brillouin-zone boundary of the original phase. A direct comparison of the phonon dispersion curves presented in Fig. 1 in Ref. 10 readily reveals that the lines at 165 cm^{-1} and 320 cm^{-1} from the IR spectra in Ref. 11 can correspond to phonons from the M point on the boundary of the original Brillouin zone and that the line at 590 cm^{-1} in the light scattering spectrum corresponds in energy to the phonon in the X point of the original Brillouin zone. Its proximity to the energy of the E_u(LO) phonon at 595 cm^{-1} is due to the weak dispersion of the latter in the $(\zeta, \zeta, 0)$ direction.[10] The doublet structure of the spectra of the electronic transitions of the Nd^{3+} ion[14] can be attributed to the lowering of the local symmetry of the environment of this ion from the $4mm$ group above T_C to the m group below T_C. The complete agreement between the data in Refs. 10 and 11 for the principal lines allowed by (1) in the IR spectra obtained at 10 K and the results of these measurements, which were performed at room temperature, can be interpreted as support for a weak temperature dependence of the phonon energies.

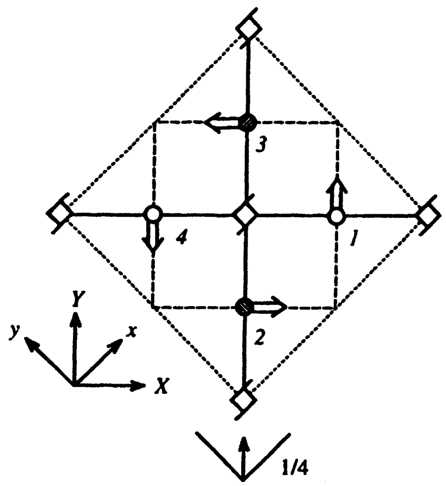

FIG. 1. Magnetic structure of Nd_2CuO_4 in the absence of structural distortions. The vertical glide planes restrict the size of the magnetic cell (only the elements which generate the $P4_2/ncm$ unitary subgroup are shown): ○—Cu ($z = c/4$); ●—Cu ($z = 3c/4$).

However, a structural phase transition is not the only possibility for allowing additional phonon lines in scattering and absorption spectra. Let us consider some other mechanisms which lead to this phenomenon.

3. INFLUENCE OF MAGNETIC ORDERING ON THE TRANSFORMATION OF THE PHONON SPECTRUM

It has been firmly established that Nd_2CuO_4 has a cross-like exchange-noncollinear magnetic structure.[3,4,6,7] In addition, the spins of the copper ions belonging to one CuO layer are ordered antiferromagnetically below $T_N = 276$ K (Ref. 7), and the antiferromagnetism vectors of neighboring layers are perpendicular to one another. Such a magnetic structure can be realized either in the presence or in the absence of structural distortions.[8,16,17] In both cases the magnetic cell contains four magnetic copper ions and, therefore, four formula units of Nd_2CuO_4. However, in the former case a structural phase transition preceded the magnetic phase transition; therefore, after the transition the magnetic cell coincides with the crystallographic cell of the $P4_2/mnm$ paramagnetic phase. In the latter case the magnetic cell is the quadrupled cell of the $I4/mmm$ paramagnetic phase.

Let us consider the transformation of the phonon absorption or scattering spectra in the absence of structural distortions after cross-like magnetic ordering with multiplication of the crystal cell. Generally speaking, in this case the vibrational spectrum, like any other excitations, must be classified among the irreducible representations of the magnetic space group or at least among the irreducible representations of the unitary subgroup. If the magnetic phase transition takes place with n-fold multiplication of the crystal cell, the new magnetic Brillouin zone will be n times smaller than the Brillouin zone of the paramagnetic phase. Consequently, excitations which had been at certain points on the boundaries of the old Brillouin zone should be found at the center of the new Brillouin zone. Therefore, determination of the points of the former Brillouin zone from which the additional branches should appear, their symmetry, and the mechanisms for their appearance in the absorption and scattering spectra, rather than the classification of the phonon spectrum among the irreducible representations of the magnetic group per se, is of interest.

The cross-like exchange-noncollinear magnetic structure shown in Fig. 1 is realized at temperatures ranging from 276 to 75 K and from 30 K to helium temperatures.[7] This structure can be formed by a second-order phase transition from the $I4/mmm$ paramagnetic phase. Then the magnetic order parameter φ is the sum of the two components

$$L_{\tau_3}(\mathbf{k}_1)=S_Y(\mathbf{k}_1)-S_X(\mathbf{k}_1),\quad L_{\tau_3}(\mathbf{k}_2)=S_Y(\mathbf{k}_2)+S_X(\mathbf{k}_2),\tag{4}$$

which have different translational symmetries. Here $S(\mathbf{k})$ is the Fourier component of the equilibrium value of the spin of the copper ion from the unit cell of the paramagnetic phase. The vectors $\mathbf{k}_1$ and $\mathbf{k}_2$, which are the rays of the $K13$ Lifshitz point of the Brillouin zone of the $I4/mmm$ group, were defined by the relation (2). Under the action of symmetry operations the components of the order parameter transform according to the τ_3 two-dimensional irreducible representation of the $K13$ star. The Cartesian components of the spins in (4) were written down in the XYZ coordinate system. The magnetic structure depicted in Fig. 1 corresponds to the order parameter φ with equal contributions from each ray, so that

$$\varphi=L_{\tau_3}(\mathbf{k}_1)+L_{\tau_3}(\mathbf{k}_2).\tag{5}$$

The magnetic symmetry group of the new phase is P_C4_2/ncm (in the x, y, and z axes). Figure 1 shows the numbering of the magnetic ions and the boundary of the new magnetic cell. As in the case of the $P4_2/mnm$ phase, which can be realized as a result of a structural phase transition,[4] the primitive translations of the P_C4_2/ncm magnetic phase, i.e., the A_i, are related to the primitive translations a_i of the paramagnetic phase by the expressions

$$A_1=a_1+a_2+2a_3,\quad A_2=a_1-a_2,\quad A_3=a_1+a_2.\tag{6}$$

The quantities a_1+a_3 and a_2+a_3 in the new phase are antitranslations. The unitary subgroup of the magnetic group is $P4_2/ncm$ (D_{4h}^{16}).

As follows from (4)–(6), the new Brillouin zone formed as a result of the $I4/mmm\rightarrow P_C4_2/ncm$ magnetic transition coincides completely with the Brillouin zone which would appear after the $I4/mmm\rightarrow P4_2/mnm$ structural transition. Therefore, after magnetic ordering, as well as after the structural transition, the phonons from the X and M points lying on the boundary of the original Brillouin zone will be at the center of the new Brillouin zone. Let us classify the phonon spectrum of Nd_2CuO_4 at these points. As will become clear from the following, there is no need for a classification according to the unitary subgroup. Calculations performed according to standard formulas (see, for example, Ref. 18) give the compositions of the mechanical representations for each ion taken individually, which are listed in Table I. The notations for the irreducible representations of each Brillouin-zone point correspond to those adopted in Ref. 15.

TABLE I.

Ion	Site	Composition of mechanical representation (group $I4/mmm$) X points ($\mathbf{k}_1$ and $\mathbf{k}_2$)	M point ($\mathbf{k}_1$ + $\mathbf{k}_2$)
Cu	$1a$	$\tau_4+\tau_6+\tau_8$	$\tau_4+\tau_{10}$
Nd	$2e$	$\tau_1+\tau_3+\tau_4+\tau_5+\tau_6+\tau_8$	$\tau_1+\tau_4+\tau_9+\tau_{10}$
O	$2c$	$2\tau_1+\tau_3+\tau_5+2\tau_7$	$\tau_4+\tau_8+2\tau_{10}$
O	$2d$	$\tau_1+\tau_2+\tau_3+\tau_4+\tau_7+\tau_8$	$\tau_1+\tau_8+\tau_9+\tau_{10}$

Using this table, we can easily see that after $I4/mmm\rightarrow P_C4_2/ncm$ magnetic ordering conforming to (5), no magnetostriction distortions corresponding to the $I4/mmm\rightarrow P4_2/mnm$ structural transition appear. In fact, the invariant of the magnetoelastic energy of the form

$$[L_{\tau_3}(\mathbf{k}_1)L_{\tau_3}(-\mathbf{k}_1)+L_{\tau_3}(\mathbf{k}_2)L_{\tau_3}(-\mathbf{k}_2)]U(0),\tag{7}$$

where $U(\mathbf{k})$ denotes some linear combinations of the Fourier components of the displacements of the ions, leads to only the isomorphic equilibrium deformations $U_{xx}+U_{yy}$ and U_{zz}. Monoclinic distortions might have appeared after the magnetic phase transition from the invariant of the form

$$L_{\tau_3}(-\mathbf{k}_1)L_{\tau_3}(-\mathbf{k}_2)U_{\tau_3}(\mathbf{k}_1+\mathbf{k}_2).\tag{8}$$

However, as follows from Table I, the mechanical representations of the M point of the Brillouin zone do not include any displacements which transform according to τ_5 irreducible representations. Therefore, if the structural distortions mentioned in Ref. 3 do, in fact, exist, despite the statements in Refs. 16 and 17, they cannot be related in any way to cross-like magnetic ordering conforming to (5).

Magnetic ordering with the formation of a cross-like structure according to the $I4/mmm\rightarrow P4_2/mnm\rightarrow P4_2/m'n'm'$ scheme[8] does not alter the number of phonon branches for $\mathbf{k}=0$ already appearing after the structural phase transition, which are specified by (3). The selection rules for the absorption and scattering of light on phonons also remain unchanged in this case.

Let us dwell in somewhat greater detail on the interpretation of the data in Ref. 14. The occurrence of the magnetic ordering of the copper ions results in removal of the Kramers degeneracy and the appearance of a doublet structure of Nd^{3+} levels both in the absence and in the presence of structural distortions. The magnitude of the splitting may be temperature-independent because at $T_N=276$ K the magnetization of the copper ion has already achieved saturation in the 10–150 K range. Of course, structural distortions cannot remove the Kramers degeneracy, but they can cause splitting of levels whose states transform according to the two-dimensional Γ_6 and Γ_7 representations. Thus, the doublet spectrum of the Nd^{3+} ion can form under the action of both the possible structural distortions and magnetic ordering of the copper subsystem. Additional measurements, for example, in a magnetic field are apparently needed for a final interpretation of the data in Ref. 14.

4. MECHANISMS OF ONE-PHONON ABSORPTION FROM THE BRILLOUIN-ZONE BOUNDARY

The influence on phonon spectra of the folding of the Brillouin zone as a result of a magnetic phase transition was investigated by Raman scattering spectroscopy in several studies, which were reviewed in Ref. 1. In this section we consider the possibility that boundary phonons may show up in infrared absorption spectra following magnetic ordering accompanied by multiplication of the crystallographic cell.

To reveal the number of phonons which are active in IR absorption after magnetic ordering, we might have restricted ourselves to an analysis of the composition of the mechanical representation on the basis of the P_C4_2/ncm Shubnikov group. However, such an approach is not constructive, since the application of an external magnetic field makes it necessary to include another Shubnikov group, which generally depends on the orientation of the magnetic field and on the rearrangement of the magnetic structure caused by it. Therefore, the further treatment will be based on the symmetry group of the paramagnetic phase. In this case any magnetic phases arising from the original paramagnetic phase can be described within a unified approach. In addition, such a treatment makes it possible to reveal the types of magnetic interactions which produce the observed effects.

In terms of the symmetry group of the paramagnetic phase, the appearance of additional lines following magnetic ordering with multiplication of the cell means that there are mechanisms which allow one-phonon absorption from the Brillouin-zone boundary of the paramagnetic phase. These mechanisms clearly appear as a consequence of the magnetic ordering. Let us first consider the electric-dipole absorption mechanism, as it is more powerful than the magnetic-dipole mechanism. According to Moriya,[19] the spin-dependent electric-dipole moment operator $\hat{P}$ of a crystal can be represented in the most general case in the form

$$\hat{P}_r(0)=\sum_{\substack{ijnm\\ \alpha\beta}} \pi^{rij}_{\alpha\beta}(n-m)\hat{S}^i_\alpha(n)\hat{S}^j_\beta(m), \tag{9}$$

where π is a parameter which depends on the Cartesian coordinates, i, j, and r label the magnetic ions in the cell, α and β are the distances between cells n and m, and $\hat{S}$ is the spin operator. Summation under the conditions $i=j$ and $n=m$ was also included in (9). A microscopic theory of the shaping of the parameters π was considered in Ref. 19. The occurrence of magnetoelastic interactions causes the parameters π to depend on the displacements of the ions from their equilibrium positions. However, unlike the ordinary magnetoelastic coupling of acoustic phonons with the magnetic subsystem, which reduces in the case of small wave vectors to different types of uniform deformation of the cell as a whole, the appearance of optical phonons or Brillouin-zone boundary phonons in the magnetoelastic interactions is highly selective. In particular, the mechanism for modulating the values of π when boundary phonons are excited can be based on variation of the strength of the exchange interactions in response to displacements of the magnetic ions themselves or in response to displacements of nonmagnetic ions which participate in a chain mediating indirect exchange. The displacements of the nonmagnetic ions which create the crystal field around a magnetic ion probably can also have a great influence. Thus, vibrations of all the ions in the magnetic material can be involved in the modulation mechanism.

We expand the parameters π in a series in the displacements of all the ions in the magnetic material and restrict ourselves to the linear terms in the expansion:

$$\hat{P}_r=\sum_{\substack{\alpha\beta\\ ijnm}} \pi^{rij}_{\alpha\beta}(n-m)\hat{S}^i_\alpha(n)\hat{S}^j_\beta(m) + \sum_{\substack{\alpha\beta\gamma\\ ijtnml}} \pi^{rijt}_{\alpha\beta\gamma}(n-m,l)\hat{S}^i_\alpha(n)\hat{S}^j_\beta(m)\hat{U}^t_\gamma(l). \tag{10}$$

Here $\pi^{rijt}_{\alpha\beta\gamma}(n-m,l)=\delta\pi^{rij}_{\alpha\beta}(n-m)/\delta U^t_\gamma(l)$, and l labels the cells. The summation over γ in (10) is carried out over all the ions in the crystallographic cell of the paramagnetic phase, and $\hat{U}$ is the ionic displacement operator, which is linear with respect to the phonon creation–annihilation operators. Going over to the Fourier representation in (10) and taking into account only the second term, for the zeroth Fourier component of the electric-dipole moment operator of the crystal we obtain

$$\hat{P}_r(0)=\sum_{\substack{\alpha\beta\gamma\\ ijtkq}} \pi^{rijt}_{\alpha\beta\gamma}(\mathbf{k},\mathbf{q})\hat{S}^i_\alpha(-\mathbf{k})\hat{S}^j_\beta(-\mathbf{q})\hat{U}^t_\gamma(\mathbf{k}+\mathbf{q}) + \sum_{\substack{\alpha\beta\gamma\\ tkq}} \pi^{rt}_{\alpha\beta\gamma}(\mathbf{k},\mathbf{q})[\hat{S}_\alpha(-\mathbf{k})\hat{S}_\beta(-\mathbf{q})]\hat{U}^t_\gamma(\mathbf{k}+\mathbf{q}). \tag{11}$$

The second term separated in (11) has an exchange origin. When the operators $\hat{S}$ are replaced by their equilibrium values S, the expression (11) describes spin-dependent one-phonon electric-dipole absorption in a magnetically ordered phase.

If this replacement is not performed, the expression specifies phonon–multimagnon absorption.[20] Such absorption was discovered in R_2CuO_4 compounds in the mid-IR region of the spectrum in Ref. 21. Phonon–two-magnon absorption appears in this range because of the large value of the integral for the intralayer exchange interaction, as well as the high density of magnon states in this region of the spectrum. A microscopic model of the formation of a multimagnon electric-dipole absorption mechanism involving phonons was considered on the basis of the three-band Hubbard model in Ref. 22. We shall not consider such many-particle absorption processes.

To take into account the symmetry, in Eq. (11) we must go over to the linear combinations of the spin operators $L_\tau(\mathbf{k})$ and the linear combinations of the displacement operators $U_\tau(\mathbf{k})$ which are basis functions of the irreducible representations of the group of the wave vector $\mathbf{k}$ in the $I4/mmm$ space group. The coefficients in them will also be linear combinations of the parameters π, for which we introduce the notation π_τ. Since we are not considering the specific microscopic mechanisms for their formation, we shall henceforth regard these coefficients as phenomenological parameters. In the case of magnetic ordering conforming to (5), the only invariant which produces one-particle one-phonon absorption from a Brillouin-zone edge in Nd_2CuO_4 is the term of the form

$$\hat{P}_r(0)=\sum_\tau \pi_\tau^{r(f)}(\mathbf{k}_1,\mathbf{k}_2)L_{\tau_3}(-\mathbf{k}_1)L_{\tau_3}(-\mathbf{k}_2)\times\hat{U}_\tau^{(f)}(\mathbf{k}_1+\mathbf{k}_2). \tag{12}$$

Here the superscript f labels the different linear combinations of U, which, however, transform according to the same irreducible representation. After diagonalization of the block of the dynamic matrix describing the interactions of vibrations of ions of the same symmetry, the superscript f will label the branches of phonons whose vibrations have the symmetry τ.

It follows from (12) that in the absence of a magnetic field the electric-dipole mechanism allows absorption by phonons only for the M point of the Brillouin-zone boundary. As a consequence of the exchange noncollinearity of the magnetic structure of Nd_2CuO_4, the exchange mechanism of electric-dipole absorption described by the second term in (11) does not make a contribution to (12).

Note that the very existence of spin-dependent one-phonon electric-dipole absorption is possible only because the magnetic phase transition is described by a multicomponent order parameter with components having different translational symmetry (corresponding to different rays of a Lifshitz point of the Brillouin zone). When the components of the order parameter have the same translational symmetry (i.e., correspond to a single ray of a multiple-ray Lifshitz point, or the point itself has only one ray), an expression like (11), in which the operators $\hat{S}$ have been replaced by the mean value S, will produce electric-dipole absorption only from the center of the Brillouin zone of the paramagnetic phase. Possibly for this reason, additional phonon absorption lines were not discovered in the absorption spectra of antiferromagnetic VI_2 below T_N, despite the efforts undertaken specially to detect them.[2] At the same time, lines corresponding to Brillouin-zone boundary phonons appeared in the scattering spectra of this crystal. It can be shown that the requirements regarding the order parameter described above are not obligatory for the manifestation of boundary phonons in the scattering spectra following a magnetic phase transition with multiplication of the unit cell.

A direct calculation of the selection rules using the data in Table I shows that the parameters $\pi_{\tau_{10}}^{X,Y(f)}(\mathbf{k}_1,\mathbf{k}_2)$ should be nonzero for X and Y polarization, and $\pi_{\tau_8}^{Z(f)}(\mathbf{k}_1,\mathbf{k}_2)$ should be nonzero for Z polarization. Thus, when unpolarized radiation is normally incident to the XY plane, the electric-dipole mechanism (12) should allow absorption by five phonons of τ_{10} symmetry from the M point of the Brillouin zone of the $I4/mmm$ group, in which vibrations of all the ions in the magnetic crystal participate. The absorption by phonons of τ_{10} symmetry, which are associated predominantly with vibrations of the copper and oxygen ions from the CuO planes, will apparently be the most intense. When the incident radiation has Z polarization, only absorption by two phonons of τ_8 symmetry, which are associated only with vibrations of oxygen ions, is possible. In this case a high intensity should be expected for the absorption by phonons associated predominantly with vibrations of the oxygen ions from the $2c$ sites, which belong to the CuO planes.

Phonons from the X points of the Brillouin zone of the $I4/mmm$ group can appear in IR absorption spectra below the Néel temperature only because of a less intense magnetic-dipole absorption mechanism. Its appearance is physically obvious. In an assigned magnetic structure of an arbitrary type, which may be either ferromagnetic or antiferromagnetic, displacements of the individual ions participating in the vibrations of optical phonons can cause distortion of the magnetic structure and the appearance of a resultant magnetic moment. The oscillation frequency of this magnetic moment is then determined by the phonon frequency. Of course, magnetic-dipole absorption by phonons whose states are t-even is possible only in the presence of magnetic order.

In the case of Nd_2CuO_4 and a magnetic structure conforming to (5), the Cartesian components of the magnetic moment operator $\hat{M}_i(\mathbf{k})$ causing one-phonon absorption from the X point of the Brillouin zone have the form

$$\hat{M}_{X,Y}(0)=\sum_f R_{\tau_7}^{X(f)}[L_{\tau_3}(-\mathbf{k}_1)\hat{U}_{\tau_7}^{(f)}(\mathbf{k}_1)\pm L_{\tau_3}(-\mathbf{k}_2)\hat{U}_{\tau_7}^{(f)}(\mathbf{k}_2)], \tag{13}$$

$$\hat{M}_Z(0)=\sum_f R_{\tau_5}^{Z(f)}[L_{\tau_3}(-\mathbf{k}_1)\hat{U}_{\tau_5}^{(f)}(\mathbf{k}_1)+L_{\tau_3}(-\mathbf{k}_2)\hat{U}_{\tau_5}^{(f)}(\mathbf{k}_2)].$$

Here the $R_\tau^{i(f)}$ are phenomenological constants. The microscopic theory for their appearance requires a separate discussion. It follows from Table I that in the case of Z polarization of the magnetic component of the incident radiation, only two phonons of τ_5 symmetry from the X point of the Brillouin-zone boundary can be excited. Both of these phonons are formed by vibrations of neodymium and oxygen ions from the CuO layers. When the radiation is normally incident to the xy plane of the sample, three phonons of τ_7 symmetry, which are formed only by vibrations of oxygen atoms, are excited by the magnetic component of the field.

We note that the magnetic-dipole absorption mechanism involving Brillouin-zone edge phonons, like Raman scattering on such phonons, will exist under any type of magnetic ordering with multiplication of the crystal cell. This is due to the linearity of the one-phonon magnetic-dipole moment operator (13) with respect to the order parameter of the magnetic phase transition.

5. ONE-PHONON ABSORPTION FROM THE BRILLOUIN-ZONE BOUNDARY IN A MAGNETIC FIELD

As follows from the treatment in Secs. 2 and 3, in Nd$_2$CuO$_4$ the $I4/mmm \rightarrow P4_2/mnm$ structural phase transition and the $I4/mmm \rightarrow P_C4_2/ncm$ magnetic phase transition, which take place with quadrupling of the unit cell, are responsible for allowing absorption by phonons from the same X and M points of the Brillouin-zone boundary of the highly symmetry $I4/mmm$ phase. However, the absorption mechanisms appearing after the magnetic phase transition are spin-dependent and, therefore, can be affected by a magnetic field. It can have a dual effect. More specifically, it can cause the appearance of new lines and the suppression of lines already existing. The former effect is trivial, since the lowering of the symmetry of a crystal in the presence of a magnetic field allows new, previously forbidden phonon lines even in nonmagnetic crystals. Suppression of the intensity of one-phonon absorption in a magnetic field is possible only when there is a spin-dependent absorption mechanism in the case of a rearrangement of the magnetic structure caused by the field.

It can be shown that the application of a magnetic field when there are structural distortions in Nd$_2$CuO$_4$ cannot result in the suppression of already existing lines. Therefore, observation of the suppression of the intensity of the one-phonon absorption in a magnetic field will unequivocally attest to a purely magnetic absorption mechanism, which appears only when there are no structural distortions in Nd$_2$CuO$_4$.

It is widely known that the most significant rearrangement of the magnetic structure of Nd$_2$CuO$_4$ occurs in a magnetic field lying in the xy plane.[6,23,24] In particular, when the field $\mathbf{H}$ is oriented parallel to the x or y axis (in the xyz coordinate system) and there are no structural distortions, the cross-like exchange-noncollinear structure collapses to an exchange-collinear structure.[24] This spin-reorientation magnetic phase transition is a second-order transition and takes place in a comparatively easily achieved magnetic field H_C.[6,24] Therefore, for simplicity we shall henceforth restrict ourselves to the case of $\mathbf{H}\|(100)$ in the xyz coordinate system [or $\mathbf{H}\|(110)$ in the XYZ coordinate system]. For a given orientation of the field the parameters in (4) depend in the following manner on the field:[24]

Phase I. $0 \leqslant H \leqslant H_C$ (exchange-noncollinear):

$$L_{\tau_3}(\mathbf{k}_1) = \sqrt{8}S\sqrt{1+\frac{H^2}{H_C^2}}, \quad L_{\tau_3}(\mathbf{k}_2) = \sqrt{8}S\sqrt{1-\frac{H^2}{H_C^2}}. \tag{14}$$

Phase II. $H_C \leqslant H \ll H_{\mathrm{ex}} \approx 10^3$ T (exchange-collinear):

$$L_{\tau_3}(\mathbf{k}_1) \approx 4S, \quad L_{\tau_3}(\mathbf{k}_2) = 0. \tag{15}$$

Here S is the mean value of the spin of the copper ion at a given temperature; the definitions of H_C and H_{ex} in terms of the parameters of the magnetic subsystem of Nd$_2$CuO$_4$ were given in Ref. 24.

Equations (14) and (15) can be used to determine the variation in the intensity of the one-phonon absorption caused by the spin-dependent mechanisms (12) and (13) as the magnetic field varies. For example, in phase I the intensity of the absorption by the phonon of the f branch from the M point of the Brillouin-zone boundary, $I_M^{(f)}$, due to the electric-dipole mechanism (12) depends on the field in the following manner:

$$I_M^{(f)} \propto [L_{\tau_3}(\mathbf{k}_1) L_{\tau_3}(\mathbf{k}_2)]^2 \propto 1 - \frac{H^4}{H_C^4}. \tag{16}$$

In magnetic fields above the phase-transition field H_C there is no absorption by phonons from the M point of the Brillouin zone. This circumstance is no accident and follows from the foregoing discussion. In fact, magnetic sublattices 1 and 3, as well as 2 and 4, become identical in fields $H \geqslant H_C$.[23,24] Formally, this means that we are dealing, so to speak, with a magnetic structure like a two-sublattice antiferromagnet placed in a magnetic field. However, such a magnetic structure can be formed from the paramagnetic phase only as a result of a phase transition described by a one-component order parameter. Therefore, according to the criterion formulated above, an electric-dipole absorption mechanism which is quadratic with respect to this parameter can produce only absorption by Brillouin-zone center phonons.

The vanishing of the component of the magnetic order parameter corresponding to the $\mathbf{k}_2$ ray of the $K13$ star in phase II causes the two previously equivalent X points of the Brillouin zone to become inequivalent. Therefore, magnetic-dipole absorption by the mechanism (13) is possible in this phase only on the phonons of the point corresponding to the $\mathbf{k}_1$ ray. The modification of the magnetic moment operator (13) for phase II follows from (15).

The application of a magnetic field results in the appearance of additional spin-dependent absorption channels. We shall consider only one of them, viz., the electric-dipole channel realized directly in phase II. It arises because the parameters π can be shaped not only by the equilibrium magnetization of the superlattices, but also by the presence of a magnetic field. Therefore, there is an electric-dipole moment associated with vibrations of the phonons from the $X(\mathbf{k}_1)$ point of the Brillouin zone, which is linear with respect to the magnetic order parameter $L_{\tau_3}(\mathbf{k}_1) \approx 4S$ and the magnetic field H. In the xyz coordinate system the Cartesian components of the operator of this electric-dipole moment have the form

$$\hat{P}_x(0) = \sum_f \tilde{\pi}_{\tau_4}^{x(f)}(\mathbf{k}_1) \cdot 4SH\hat{U}_{\tau_4}^{(f)}(\mathbf{k}_1),$$

$$\hat{P}_y(0) = \sum_f \tilde{\pi}_{\tau_6}^{y(f)}(\mathbf{k}_1) \cdot 4SH\hat{U}_{\tau_6}^{(f)}(\mathbf{k}_1), \tag{17}$$

$$\hat{P}_z(0)=\sum_f \tilde{\pi}_{\tau_2}^{z(f)}(\mathbf{k}_1)\cdot 4SH\hat{U}_{\tau_2}^{(f)}(\mathbf{k}_1).$$

We note that phonons with odd states relative to the spatial inversion operation are excited through electric-dipole absorption from both the M point (12) and from the $X(\mathbf{k}_1)$ point of the Brillouin zone.

From the experimental standpoint it is interesting that vibrations of the copper and neodymium ions should be excited in a magnetic field when the radiation is normally incident to the xy plane (see Table I). Since the neodymium ion is the heaviest ion in the composition of Nd_2CuO_4, it would be expected that the lowest-energy phonons from the X point of the Brillouin zone correspond to it.[10]

6. EXPERIMENTAL METHOD

The effects of the transformation of the phonon spectra of crystals arising from multiplication of the unit cell as a result of a structural or magnetic phase transition were investigated using a Fourier spectrometer with a measuring cell which permits cooling of the sample under investigation to liquid-nitrogen temperatures and does not contain additional windows. Since Nd_2CuO_4 crystals are practically opaque in the far-infrared region of the spectrum, the reflectance spectra were recorded in the experiment and were then treated using the Kramers–Kronig procedure. We investigated the reflectance spectra from the xy plane of the sample with almost normal incidence. In this geometry only lines associated with the appearance of the x and y components of the electric- and magnetic-dipole moment should be observed.

The Fourier spectrometer used is a completely automated instrument that includes an opticomechanical section and a control system.

The opticomechanical section of the instrument consists of three separately evacuated chambers: an interferometer chamber, a sample chamber, and a detector chamber. The interferometer chamber contains a radiation source and a symmetric Michelson interferometer with interchangeable beam splitters. A 220-W mercury lamp serves as the radiation source. The lamp is placed in a water-cooled housing having three switchable diaphragms with diameters equal to 3, 5, and 10 mm. The diaphragms are used to adjust the intensity of the radiation. Mirrors with a diameter of 60 mm and a thick-layer aluminum coating are employed in the instrument. Mylar films of various thicknesses from 6 to 50 μm serve as beam splitters, which make it possible to obtain spectra in the range from 10 to 570 cm^{-1}. The movable mirror of the interferometer is displaced by a micrometer screw, which makes it possible to vary the optical path from -10 to $+10$ cm, providing for the recording of spectra with a maximum resolution of 0.1 cm^{-1}. A raster system based on metrological gratings, which provides for a resolution of 2 μm, is employed to accurately determine the position of the mirror. The rate of displacement of the movable mirror can be varied over a broad range from 1.25 to 640 μm/s, making it possible to optimize the measurement time in accordance with the spectral range and the required resolution in the spectrum. The sample chamber contains a cooled sample cell and a focusing mirror system with remote-control configuration variation, which makes it possible to record both transmission spectra and reflectance spectra. The detector chamber contains an output focusing mirror, a unit for switching the optical filters, and a cooled detector. The vacuum system of the instrument makes it possible to separately evacuate each of the chambers to pressures of the order of 1 Pa, making it possible to eliminate atmospheric absorption (by water vapor).

The detector used for infrared radiation was a nonisothermal superconducting bolometer. Its integral conversion coefficient was equal to 10^4 V/W in a dynamic range with a width of 2×10^5. Such a broad dynamic range is necessary, in principle, for the detector in a Fourier spectrometer, since distortions of the interferogram result not only in amplitude distortions, but also in frequency distortions of the spectra recorded. The employment of a superconductor bolometer permitted improvement of the signal-to-noise ratio by more than an order of magnitude when the weak lines in the spectra of Nd_2CuO_4 were investigated. The external magnetic field was created by samarium–cobalt magnets. The maximum field strength was 0.2 T.

Let us examine the conditions under which the experiment was carried out. As follows from Secs. 4 and 5, all the spin-dependent mechanisms for the appearance of absorption from the Brillouin-zone boundary are determined by the value of the magnetization of the copper ions. In order for it to practically achieve saturation at $T_N=276$ K, it is sufficient to lower the sample temperature to 100–150 K. Taking into account that a spin-reorientation transition takes place at 75 K in Nd_2CuO_4, the measurements were performed at 150 K to simplify the analysis. According to the data in Refs. 6 and 25, the transition field strength H_C was equal to 0.2 T at $T=10$ K. At 150 K its value was very small, so that this transition was certainly completed in an external field with a strength of 0.05 T.

The samples were prepared from high-quality single crystals grown by controlled crystallization with a solution–melt interface and had the form of plates having an area of 5×5 mm^2 with the fourth-order axis perpendicular to their surface.[1)]

7. EXPERIMENTAL RESULTS

The reflectance spectrum of Nd_2CuO_4 at 90 K in the absence of an external magnetic field is presented in Fig. 2. As a whole, it coincides with the spectrum at 10 K presented in Ref. 11 [Fig. 3(a)] for the same experimental geometry. A comparison of our data and the data in Ref. 11 with the results of the inelastic neutron scattering experiments at room temperature in Ref. 10 reveals that the spectral positions of the lines of the ground-state E_u phonons corresponding to the high-temperature $I4/mmm$ phase [see Eq. (1)] and the neutron peaks of the same symmetry from the Γ point of the Brillouin zone practically coincide. The weak temperature dependence of the energy of the ground-state phonons in Nd_2CuO_4 enables us to use the data in Ref. 10 to identify the Brillouin-zone boundary phonons displayed in the spectra after multiplication of the unit cell.

Our spectra, like the spectra in Ref. 11, displayed several weak lines which do not fit the classification (1). Their ap-

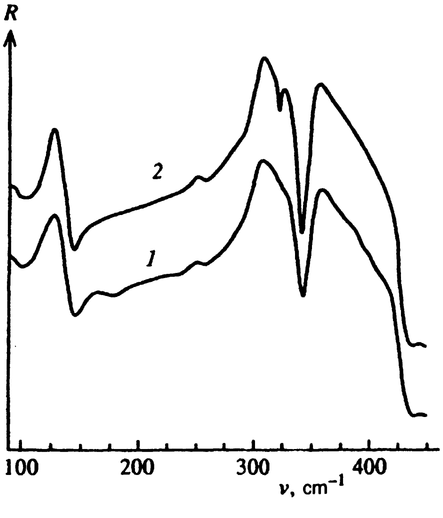

FIG. 2. Reflectance spectra of Nd_2CuO_4 at 150 K: *1)* $H=0$; *2)* $H=0.05$ T.

pearance can be caused by either a structural (Sec. 3) or a magnetic (Secs. 4 and 5) phase transition. The only possibility for establishing the cause of the appearance of these lines is to perform measurements in an external magnetic field. Its value should exceed the value of H_C which transformed the exchange-noncollinear magnetic structure into an exchange-collinear structure. We performed such measurements, which showed that the influence of an external field applied along the (100) axis in the xyz coordinate system is "sensed" by the lines at 170 cm^{-1} and 320 cm^{-1}. These frequencies do not correspond to any of the vibrational frequencies with E_u symmetry listed in Ref. 11. The portions of the absorption spectra Im(ϵ) corresponding to them are presented in Fig. 3. According to our data, the lines of the ground-state phonons of E_u symmetry are not affected by a magnetic field.

The variation of the intensity of the lines at 170 cm^{-1} and 320 cm^{-1} in the presence of an external magnetic field unequivocally attests to the absence of structural distortions in Nd_2CuO_4, at least at temperatures above 150 K. The phonon dispersion curves presented in Ref. 10 show that these lines can correspond to one-phonon absorption from both the X and M points of the Brillouin zone of the $I4/mmm$ phase. Since the line at 170 cm^{-1} is suppressed by the external field, it "originates," according to (16) and (17), from the M point, and the line appearing in the field at 320 cm^{-1} originates from the X point of the Brillouin zone.

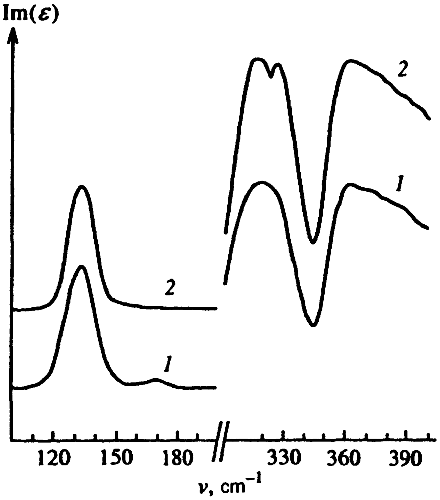

FIG. 3. Absorption lines at 170 cm^{-1} and 320 cm^{-1}, which "sense" a magnetic field: *1)* $H=0$; *2)* $H=0.05$ T.

Let us discuss the possibility of a different interpretation for the results obtained. A many-particle origin is unlikely for the new lines which we observed, since, despite the fairly high temperature of 150 K, the widths of these lines and the lines of the ground-state E_u phonons are comparable to one another and to the widths of the lines observed in Ref. 11 at 10 K. Bands of magnon–phonon absorption can be ruled out by the anomalously large dispersion of the spin waves in the direction parallel to the CuO layers.[26] Two-phonon absorption bands should have a fairly large width and should be located in a different frequency range. Among the lowest energy levels of the Nd^{3+} ion determined by the crystal-field-split ground-state multiplet, there is a Kramers doublet corresponding to the $\Gamma_6 \rightarrow \Gamma_7$ transition, which is close in energy to 170 cm^{-1} (Ref. 27). At 150 K this doublet has splitting of the order of 5 ± 1 cm^{-1} owing to the copper–neodymium interaction.[14] The magnitude of the splitting is determined by the absolute value of the magnetization of the copper ion and therefore does not depend on the rearrangement of the magnetic structure of the copper subsystem. Such splitting was not observed in our experiments. In addition, the position of this level of the Nd^{3+} ion is determined by the strength of the crystal field; therefore, the mechanisms for its excitation cannot be spin-dependent and certainly not dependent on the relative orientation of the spins of the copper ions. There is one more argument in favor of the phonon origin of the line at 170 cm^{-1} in our spectra. In Ref. 4 an excitation with a similar frequency was observed by Raman scattering spectroscopy; therefore, in a crystal with the D_{4h} symmetry point group such an excitation cannot be exhibited in the IR spectra because of the alternative prohibition rule. There is no energy level close to 320 cm^{-1} in the spectrum of the Nd^{3+} ion.

We suggest that the main mechanism for absorption from the Brillouin-zone boundary is the electric-dipole mechanism. It is seen from the data in Ref. 11 that the entire phonon spectrum of Nd_2CuO_4 is located along the energy scale in the 0–600 cm^{-1} range. It would be expected that its high-frequency portion is shaped predominantly by vibrations of the lightest ions, i.e., the oxygen ions, and that its low-frequency portion is shaped by vibrations of the heaviest ions, i.e., the neodymium ions. The vibrations from the middle of the range indicated, which correspond mostly to vibrations of the magnetic copper ions, turned out to be most sensitive to the occurrence of magnetic ordering and to the application of a magnetic field. The displacements of just these ions should have had the most significant effect on the shaping of the parameters π. In this case the energies of the phonons are weakly dependent on the occurrence of magnetic ordering. This makes it possible to base the interpretation of absorption experiments on the symmetry group of the paramagnetic phase and to regard the occurrence of magnetic ordering as a weak perturbation.

8. CONCLUSIONS

An investigation of the behavior of the magnetic subsystem can serve as a test for the presence or absence of structural distortions. In particular, the linear magnetoelectric effect in Nd_2CuO_4 predicted in Ref. 8 was not observed in Ref. 28. Since this effect is possible only in the presence of structural distortions, this can be evidence in support of their absence. However, to make a final statement, measurements of the phonon spectra must be carried out over a broad temperature range. For example, the behavior of the lowest-energy phonon mode from the X point of the Brillouin zone of Nd_2CuO_4 was studied by inelastic neutron scattering spectroscopy in Ref. 29 at lower temperatures than in Ref. 10. Although no significant suppression of the modes was observed in that work, the tendency for instability of the CuO layer toward rotation around the c axis was maintained over the entire temperature range investigated. At $T=5$ K anomalies were observed in the elastic properties of Nd_2CuO_4, which can attest to alteration of the magnetic structure.[25] The situation becomes more complicated at lower temperatures, after ordering of the magnetic subsystem of the neodymium ions. Thus, the data from the measurements in Refs. 25 and 30 indicate the occurrence of a whole series of magnetic phase transitions in this temperature range.

Our measurements can also serve as evidence of the existence of a cross-like exchange-noncollinear magnetic structure in Nd_2CuO_4. This is because the observation of one-phonon absorption from the Brillouin-zone boundary of the paramagnetic phase in the absence of a magnetic field is possible only if the magnetic structure is described by a two-component order parameter with different translational symmetries for the components and is consequently exchange-noncollinear. Additional support is also provided by the characteristic behavior of the absorption spectra of the boundary phonons in a magnetic field.

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