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Symmetry analysis of multiferroic Co_3TeO_6

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A phenomenological explanation of the magnetoelectric behavior of Co_3TeO_6 is developed. We explain the second harmonic generation data and the magnetic field induced spontaneous electric polarization in the magnetically ordered phase below 20 K.

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I. INTRODUCTION

Recently there has been an explosion in the number of compounds which exhibit nontrivial magnetoelectric behavior at low temperatures.[1–5] Co_3TeO_6 (CTO) is an interesting such system whose properties have recently been studied.[6] Although the magnetic structure is as yet unclarified, it seems useful to construct a mean-field scenario which can explain the major experimental results. The measurements of Hudl *et al.*[6] of M/H, $d(M/H)/dT$, and C/T versus T, where M is the magnetization, H the magnetic field, and C the specific heat, indicate that there are at least two magnetic phase transitions at temperatures below about 30 K, one at $T_1 \approx 26$ K and another at $T_2 \approx 18.5$ K, but the details of the magnetic structure are not known, other than that the system is not ferromagnetic. According to Ref. 7, the magnetic structure is described by several incommensurate wave vectors. Single-crystal neutron diffraction measurements[8] reveal that the incommensurate wave vector(s) are in the *a*-*b* plane and not along *c*. We propose the existence of magnetic order at zero wave vector (involving an antiferromagnetic arrangement of moments within the unit cell to give the observed zero net moment) and the appearance of an additional magnetic phase transition, both consistent with Refs. 7 and 8. For $T > 30$ K the crystal symmetry is[6,9] that of space group $C2/c$ (no. 15 in Ref. 10). We take the generators of this space group to be the glide operation $m_b \equiv (x,-y,z+1/2)$, a twofold screw rotation about the crystal b axis, $2_b \equiv (-x,y+1/2,-z+1/2)$, and the three translations $(x+1/2,y+1/2,z)$, $(x-1/2,y+1/2,z)$, and $(x,y,z+1)$, where x, y, and z are in units of lattice constants. These are equivalent to those of Ref. 11.

II. EXPERIMENTAL DATA

The data of Hudl *et al.*[6] consist of several types. As mentioned above, the measurements of magnetization and specific heat indicate phase transitions at at least two temperatures, T_1 and T_2, but the nature of magnetic ordering could not be determined from their data. The lower-temperature transition may be a discontinuous one. Of primary interest to us is their measurement of the intensity of second harmonic generation (SHG), whose cross section is proportional to the third-order electric susceptibility $\chi_{\alpha\beta\gamma}$, where α, β, and γ label components (or in the present case, label crystallographic directions). Their experimental geometries are chosen such that the SHG cross section is proportional to $\chi_{\alpha\alpha\alpha}$. In a system having high symmetry, e.g., having inversion symmetry, the SHG intensity is zero for all frequencies, and this applies to CTO above about $T_2 = 18.5$ K. However, below that temperature they find that χ_{aaa} and χ_{ccc} are nonzero, but χ_{bbb} is apparently zero at all temperatures. From this they conclude that the point group retains only m_b symmetry. As we shall see, if, as they assert, the symmetry is magnetically broken, this is not a correct conclusion.

Another type of data of crucial interest to us are the measurements of the electric polarization $\mathbf{P}$ in the *a*-*c* plane as a function of temperature and magnetic field for magnetic fields along the a and c directions. For zero magnetic field, at temperatures below about 18 K they find a very small, possibly zero, spontaneous polarization in the a and c directions which increases almost proportional to the magnetic field. In fact, we find that their results for P_c at $T = 5$ K as a function of H_a can be fit within experimental uncertainty (± 5 in P_c) to

$$P_c = -0.15 + 6.93H_a + 0.33H_a^2, \qquad (1)$$

with P_c in μC/m^2 and H_a in Tesla. In other words, they found an important magnetic field-dependent contribution to P_c linear in H_a with $P_c(H_a = 0) \approx 0$.

III. SYMMETRY ANALYSIS

We will carry out our analysis in terms of an expansion about the “vacuum,” which we take to be the phase above 26 K in which the magnetic order parameters and electric polarization are zero. Magnetically ordered phases are described by nonzero magnetic order parameters. We will also discuss briefly nonmagnetic structural distortions which lower the crystal symmetry from $C2/c$ and which are described by appropriate order parameters. Although, as mentioned in Ref. 6, there may exist incommensurate magnetic order described by $\mathbf{M}(\mathbf{q})$ with $q \neq 0$, incommensurate magnetic order cannot, by itself, explain the experimental results, as we will explain below.

A. Electric Polarization

We first review the phenomenological theory of magnetization-induced electric polarization $\mathbf{P}$. The magnetoelectric free energy is of the form

$$F_{\rm ME} = \frac{1}{2}\chi_E^{-1}\mathbf{P}^2 + \sum_n \Delta F^{(n)}, \qquad (2)$$

where χ_E is the dielectric susceptibility of the vacuum (the phase above $T = 26$ K), which we assume to be isotropic for simplicity, and $\Delta F^{(n)}$ is the contribution linear in $\mathbf{P}$ (so that it induces a nonzero value of $\mathbf{P}$) and of order H^n. For instance, to lowest order in powers of the magnetic order parameters, we write[5,12]

$$\begin{aligned}\Delta F^{(0)} &= \sum_{\mathbf{q}\neq 0} a_{\alpha kl}(\mathbf{q}) P_\alpha [M_k(\mathbf{q})^* M_l(\mathbf{q}) - M_k(\mathbf{q}) M_l(\mathbf{q})^*] \\ &\quad + b_{\alpha kl} P_\alpha M_k(q=0) M_l(q=0), \\ \Delta F^{(1)} &= c_{\alpha\beta k} P_\alpha H_\beta M_k(q=0), \\ \Delta F^{(2)} &= \sum_{\mathbf{q}\neq \mathbf{0}} d_{\alpha\beta\gamma kl}(\mathbf{q}) P_\alpha H_\beta H_\gamma \\ &\quad \times [M_k(\mathbf{q})^* M_l(\mathbf{q}) - M_k(\mathbf{q}) M_l(\mathbf{q})^*] \\ &\quad + e_{\alpha\beta\gamma kl} P_\alpha H_\beta H_\gamma M_k(q=0) M_l(q=0), \end{aligned} \tag{3}$$

where we invoke the Einstein convention which implies summation over repeated subscripts, Greek subscripts label crystallographic directions, and Roman letters label irreducible representations (irreps), which in the present case are one dimensional. The magnetic order parameter $M_k(\mathbf{q})$ can be thought of as the amplitude of the magnetic normal mode associated with irrep Γ_k.[5] These normal modes are the linear combinations of magnetic moments within the unit which bring the quadratic terms in the Landau expansion into diagonal form. We will discuss the symmetry of the M_k's in a moment. Here the Fourier transforms are defined so that for $\mathbf{q} \neq 0$, $\mathcal{I} M_k(\mathbf{q}) = M_k(\mathbf{q})^*$, where $\mathcal{I} = m_b 2_b$ is a spatial inversion.

F_{ME} must be invariant under all the symmetries of the "vacuum." These symmetries include time reversal symmetry, translational symmetry (which leads to wave vector conservation), and the crystallographic symmetries m_b and 2_b (which together imply invariance under spatial inversion $\mathcal{I}$). We will consider the crystallographic symmetries in a moment. Time reversal symmetry requires that the total number of powers of H and $M(\mathbf{q})$ must be even. The condition that F_{ME} be real valued implies that $\mathbf{a}(\mathbf{q})$ and $\mathbf{d}(\mathbf{q})$ be purely imaginary. The form of $\Delta F^{(1)}$ is such that wave vector conservation implies that the magnetic order for this mechanism must occur at zero wave vector, and, as previously noted, it must be antiferromagnetic to be consistent with the observed zero net magnetic moment of the system. (In fact, CTO has a large enough paramagnetic unit cell that antiferromagnetic order can develop without increasing the size of the unit cell, as occurs in $LaTiO_3$[13] and Cr_2O_3.[14]) Such an antiferromagnetic moment would be consistent with the magnetic measurements of Hudl *et al.*.[6]

When F_{ME} is minimized with respect to $\mathbf{P}$ to obtain its equilibrium value, one sees that $\Delta F^{(n)}$ gives rise to a contribution to $\mathbf{P}$ which is of order H^n. In many multiferroics, such as $Ni_3V_2O_8$[2,4] (NVO) and $TbMnO_3$[3] (TMO), $\Delta F^{(0)}$ is a crucial term which gives rise to a spontaneous polarization at $H = 0$. Many other cases are similarly analyzed in Ref. 5. In these cases, the magnetic order is incommensurate, so that the polarization (a zero wave vector property) cannot be linear in the magnetic order parameter. Since in CTO $P \propto H$, we consider $\Delta F^{(1)}$, using which we get

$$P_\alpha = \chi_E \sum_{\beta k} c_{\alpha\beta k} H_\beta M_k. \tag{4}$$

We now show how the crystallographic symmetries constrain the coefficient tensor $c_{\alpha\beta k}$. In particular, we will show that these symmetries fix the symmetry of M_k. For this purpose, note that $\Delta F^{(1)}$ has to be invariant under these symmetries. In this analysis, we will confine $\mathbf{P}$ and $\mathbf{H}$ to be perpendicular to the crystallographic $\mathbf{b}$ direction, as they were in the experiments of Ref. 6. In that case, we only consider terms in $\Delta F^{(1)}$ with α and β labeling the crystallographic a and c directions, and k labels the possible magnetic irreps at zero wave vector. Remembering that $\mathbf{H}$ is a pseudovector, we note that

$$m_b[P_\alpha H_\beta] = -P_\alpha H_\beta, \qquad 2_b[P_\alpha H_\beta] = P_\alpha H_\beta. \tag{5}$$

Accordingly, for $\Delta F^{(1)}$ to be an invariant we require that

$$m_b M_k = -M_k, \quad 2_b M_k = M_k. \tag{6}$$

TABLE I. Symmetry of the magnetic irreps Γ_n at zero wave vector for CTO. Here $\lambda(\mathcal{O})$ is the eigenvalue of the operator $\mathcal{O}$: $\mathcal{O}M_k = \lambda(\mathcal{O})M_k$, where $M_k = M(\Gamma_k)$ is the order parameter associated with the kth irrep. Also $\mathcal{E}$ is the identity and $\mathcal{I}$ is spatial inversion. In the last line, we give the direction of the ferromagnetic moment if it is allowed to be nonzero.

	Γ_1	Γ_2	Γ_3	Γ_4
$\lambda(\mathcal{E})$	+1	+1	+1	+1
$\lambda(2_b)$	+1	+1	−1	−1
$\lambda(m_b)$	+1	−1	−1	+1
$\lambda(\mathcal{I})$	+1	−1	+1	−1
$\vec{M}$	$\vec{b}$	0	$\perp b$	0

To implement Eq. (6), we need to characterize the symmetry of the magnetic ordering, which we have inferred occurs at zero wave vector. For phase transitions the catalog of broken symmetry phases that can result from a phase transition in any of the 230 crystallographic space groups can be obtained using the suite of computer programs ISODISTORT, which is accessible on the web.[15] As applied to CTO one predicts that only four magnetic irreps can result from a single phase transition at zero wave vector. This formulation specifically does not allow for a multicritical point at which there is a simultaneous breaking of two distinct symmetries. For CTO there is no experimental indication that the magnetic phase transitions arise from such a multicritical point.[16] Therefore we assume the validity of the four possible magnetic phases of Table I which ISODISTORT lists for space group $C2/c$. Looking at Table I we see that to be consistent with Eq. (6), the magnetic order parameter can only be that of irrep Γ_2.

B. Second Harmonic Generation

We now turn to the analysis of the SHG cross section at $H = 0$. To develop a nonzero SHG cross section a quantity like $\partial\chi_{\alpha\alpha\alpha}/\partial M_\beta$ must be nonzero in the vacuum (magnetically disordered phase), so that when we turn on the magnetic order parameter M_β (in the magnetically ordered phase) the SHG cross section becomes nonzero. To study this quantity it is useful to note that it has the symmetry of $\partial[p_\alpha p_\alpha p_\alpha]/\partial M_k$, where p_α is the α component of the dipole moment operator and M_k is a magnetic order parameter. One sees that this quantity is zero because M_k is odd under time reversal and the dipole moment operator is even under time reversal.[17] Therefore, the phenomenological explanation for a nonzero SHG cross

TABLE II. As Table I. Symmetry of the product of two zero wave vector magnetic irreps Γ_n for CTO.

	$\Gamma_1\Gamma_2$	$\Gamma_1\Gamma_3$	$\Gamma_1\Gamma_4$	$\Gamma_2\Gamma_3$	$\Gamma_2\Gamma_4$	$\Gamma_3\Gamma_4$
$\lambda(2_b)$	+1	−1	−1	−1	−1	+1
$\lambda(m_b)$	−1	−1	+1	+1	−1	−1

section must come from $X_\alpha \equiv \partial^2[p_\alpha p_\alpha p_\alpha]/[\partial M_k(\mathbf{q})\partial M_l^*(\mathbf{q})]$ being nonzero in the disordered phase. This quantity has the same symmetry as $X_\alpha \equiv p_\alpha^3\mathcal{M}$, where $\mathcal{M} = M_k(\mathbf{q})M_l^*(\mathbf{q})$ or $\mathcal{M} = M_kM_l$. The fact that the SHG is proportional to the product of two different order parameters, each of which, as we shall see, describes a one-dimensional irrep, has been noted before.[18] Here, from the polarization data, we know of the existence of at least one irrep at zero wave vector, and according to Ref. 7, magnetic ordering occurs with at least one irrep at nonzero wave vector. To have a nonzero SHG cross section we need a second irrep, either at zero wave vector or at the same nonzero wave vector. In either case the appearance of a second irrep requires an as yet unobserved phase transition, which may be unobtrusive enough that it was not seen by Hudl *et al*. We consider these two scenarios in turn.

The condition for a nonzero SHG cross section is identical to that for a nonzero electric polarization because the symmetry properties of the dipole moment operator and the electric polarization are the same. Thus, if χ_{aaa} and χ_{ccc} are nonzero, then P_a and P_c are expected to be nonzero. Furthermore, no matter which scenario is adopted, there is a possible problem in that although experiments show that for $H = 0$, χ_{aaa} and χ_{ccc} are nonzero and $\chi_{bbb} = 0$, the expected field-independent contributions to P_a and P_c are very small. The explanation for this may be that the SHG is anomalously large when the polarization is due to modification of electronic orbits (as contrasted to being due to ionic displacements).[21]

In the first scenario, we assume that the nonzero SHG cross section is induced by magnetic order at zero wave vector and study the symmetry properties of X_α. Since p_α^2 transforms like unity, it suffices to study $X_\alpha \equiv p_\alpha M_kM_l$ to indicate whether $\chi_{\alpha\alpha\alpha}$ is or is not zero. Since $\chi_{bbb} = 0$, we require that $p_bM_kM_l$ be odd under either m_b or 2_b. This implies that M_kM_l either be even under m_b or odd under 2_b. Using Table II, we see that this criterion excludes either M_1M_2 or M_3M_4 being nonzero. Similarly, if χ_{aaa} and χ_{ccc} are nonzero, we require that both $p_aM_kM_l$ and $p_cM_kM_l$ be even under both m_b and 2_b. This implies that M_kM_l be even under m_b and odd under 2_b. These requirements indicate that either M_1M_4 or M_2M_3 be nonzero. Since we have previously invoked the existence of irrep M_2 to explain the electric polarization, we opt for M_2M_3 being nonzero. The fact that the magnetic moment perpendicular to b (coming from irrep M_3) is zero (or very small) would have to be a result specific to the details of the interactions.

In the second scenario one would have to posit an additional phase transition involving a second incommensurate magnetic irrep to give rise to a nonzero SHG cross section. In principle, one would have an accompanying field-independent polarization coming from $\Delta F^{(0)}$, whose absence in experiment would have to be explained as above in terms of an unusually large SHG cross section. To illustrate this mechanism, consider the hypothetical case when the incommensurate magnetic ordering occurs at $\mathbf{q} = q_0\hat{b}$. In this case one finds that there are two magnetic irreps, one of which, call it $M_1(\mathbf{q})$, is even under 2_b and the other, call it $M_2(\mathbf{q})$, is odd under 2_b. Then one sees that $X \equiv p_a[M_1(\mathbf{q})^*M_2(\mathbf{q}) - M_1(\mathbf{q})M_2(\mathbf{q})^*]$ and $Y \equiv p_c[M_1(\mathbf{q})^*M_2(\mathbf{q}) - M_1(\mathbf{q})M_2(\mathbf{q})^*]$ are both invariant under 2_b (and under $\mathcal{I}$), so that $\chi_{aaa} \propto X$ and $\chi_{ccc} \propto Y$ are allowed to be nonzero, whereas χ_{bbb} remains zero. In a common scenario[5] one irrep would give rise to nonzero magnetic moments along the $\hat{b}$ axis and the other would give rise to nonzero magnetic moments along the c axis. These irreps would be out of phase [so that $M_1(\mathbf{q})^*M_2(\mathbf{q}) - M_1(\mathbf{q})M_2(\mathbf{q})^*$ is nonzero], giving rise to a magnetic spiral.[19]

C. Discussion

To summarize our conclusions, we require the existence of zero wave vector magnetism according to irrep M_2 to explain the magnetic field induced electric polarization. In one scenario we explain the SHG cross section as being proportional to M_2M_3. Since we prefer not to assume a multicritical point, the latter result would imply that there are actually two phase transitions. At the higher-temperature transition (at $T = 18.5$ K) a magnetic field induced spontaneous electric polarization appears and at the lower-temperature transition (at some temperature close to but below 18.5 K) the SHG cross section becomes nonzero. Here a very small magnetic field independent polarization should also appear. In principle, one would hope to show the temperature dependence of the SHG cross section to be proportional to the product of these two order parameters whose temperature dependence was independently established by neutron diffraction. This type of experimental program was carried out for the electric polarization of NVO (see Fig. 6 of Ref. 20). Note also a magnetically induced SHG cross section implies that the symmetry involves time reversal. The magnetic phase with irrep M_2 is *odd* under m_b, as indicated in Table I. In contrast, if we were dealing with a nonmagnetic structural phase transition, as the analysis of Hudl *et al*. tacitly assumes, then the low-temperature phase would be even under m_b, as they state. However, note that the presence of magnetic irreps M_2 and M_3 breaks the mirror symmetry of m_b, but the symmetry of m_b plus time reversal is maintained. This is consistent with the results of Tables 7 and 4 of Ref. 22. (The misidentification of Ref. 6 is not completely harmless. If one assumes that m_b symmetry is unbroken, then, as they find, it is impossible to use $\Delta F^{(1)}$ to explain why $\partial P_\alpha/\partial H_\beta$ is nonzero for $\alpha,\beta = a,c$.)

The second scenario has similar ramifications except that it involves magnetic ordering at some incommensurate wave vector. This scenario would also require a second phase transition at which a second incommensurate order parameter would appear.[23] In principle, such a transition could involve a slightly different wave vector than that already present. But, as argued in Ref. 4, quartic terms in the Landau free energy would favor locking these two nearby wave vectors to the same value.

We have implicitly assumed that the experimental results are induced by magnetic ordering. One might question whether the results of Ref. 6 could be explained by simply invoking one or more phase transitions driven by structural distortions. Since magnetic ordering appears at these transitions, the question is which order parameter is the primary one whose presence induces the appearance of the other one. If Q is a structural order parameter (like the tilting angle of a cage of oxygen ions), then one can invoke an interaction of the type $V \sim M(\Gamma_k)M(\Gamma_l)Q$ to explain the appearance of a nonzero value of Q at the transition. Via this coupling the appearance of one or more magnetic order parameters (which are the primary order parameters) would induce a structural distortion (because Q appears linearly). The converse case, where the magnetic order parameter appears linearly and the primary order parameter Q appears quadratically (or linearly, for that matter) is not allowed by time reversal symmetry. But if the magnetic order parameters are the primary ones, then the theoretical approach of the present paper is essentially unchanged by the appearance of secondary structural order parameters.

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