

## Theory of nonreciprocal optical effects in antiferromagnets: The case of $\text{Cr}_2\text{O}_3$

V. N. Muthukumar, Roser Valentí, and Claudius Gros

*Institut für Physik, Universität Dortmund, D-44221 Dortmund, Germany*

(Received 4 October 1995)

A microscopic model of nonreciprocal optical effects in antiferromagnets is developed by considering the case of  $\text{Cr}_2\text{O}_3$  where such effects have been observed. These effects are due to a *direct* coupling between light and the antiferromagnetic order parameter. This coupling is mediated by the spin-orbit interaction and involves an interplay between the breaking of inversion symmetry due to the antiferromagnetic order parameter and the trigonal field contribution to the ligand field at the magnetic ion. We evaluate the matrix elements relevant for the nonreciprocal second harmonic generation and gyrotropic birefringence. [S0163-1829(96)05322-2]

### I. INTRODUCTION

The study of optical phenomena in magnetic substances has always been an interesting area of research. Optical effects exhibited by magnetic substances can be classified broadly into two categories, reciprocal and nonreciprocal.<sup>1</sup> Reciprocal optical phenomena are those that cannot distinguish between magnetic states that are related to one another by time reversal. Typical examples of such phenomena are those that involve scattering of light by magnetic excitations. Nonreciprocal phenomena, on the other hand, can distinguish between two magnetic states that are related to each other by time reversal. A classic example of such a phenomenon is the Faraday effect discovered by Faraday in the last century. The Faraday effect in ferromagnets, for instance, appears as a rotation of the plane of polarization of light which is incident along the axis of magnetization. This rotation is nonreciprocal in the sense that it changes sign on reversing the direction of magnetization (which is equivalent to time reversal). Such an effect can be understood in terms of an interaction between the internal molecular field of the ferromagnet and the incident electromagnetic radiation mediated by the spin-orbit coupling.<sup>2</sup> Clearly, such an effect would not only be exhibited by ferromagnets but by any substance that has a net (nonzero) magnetic moment such as ferrimagnets or paramagnets where a magnetic moment is induced by the application of an external field.

It is then but natural to ask what happens in the case of antiferromagnets. At first sight, it would seem that it is impossible for light to distinguish between states that are related by time reversal as, in this case, there is no net magnetic moment (i.e., the total molecular field is zero unlike in ferromagnets). However, this is not true. In fact, it has been known for a long time from symmetry arguments that certain classes of antiferromagnets can show a variety of nonreciprocal phenomena,<sup>3,4</sup> although till recently, there have been no reports of experimental observations of such phenomena. The utility of such experiments, where possible, can hardly be overemphasized since experiments such as Raman scattering, etc., only probe the antiferromagnetic structure *indirectly* by coupling to the magnetic excitations rather than the magnetic ordering itself.<sup>5</sup>

In this context therefore, the discovery of nonreciprocal optical effects below the Néel temperature  $T_N$  in optical ex-

periments on  $\text{Cr}_2\text{O}_3$  (Refs. 6 and 7) comes as a breakthrough in the study of antiferromagnetic ordering by light. Krichevstov *et al.*<sup>6</sup> reported the experimental observation of spontaneous nonreciprocal rotation and circular dichroism below the Néel temperature of  $\text{Cr}_2\text{O}_3$ . Fiebig *et al.*<sup>7</sup> found that antiferromagnetic domains could be observed *directly* by nonreciprocal second-harmonic generation (SHG), leading to photographs of antiferromagnetic domains.<sup>8,9</sup> These experiments show that light can indeed couple directly to the antiferromagnetic order parameter, thereby leading to nonreciprocal effects. As mentioned earlier, though such a coupling was anticipated from symmetry considerations, no microscopic mechanism has been presented so far.

In this paper, we present, in detail, a microscopic mechanism that describes all nonreciprocal optical effects by considering the case of  $\text{Cr}_2\text{O}_3$  where such effects have been observed experimentally. In an earlier paper,<sup>10</sup> we showed that all nonreciprocal effects in  $\text{Cr}_2\text{O}_3$  can be explained by the fact that *electric dipole* transitions are allowed in  $\text{Cr}_2\text{O}_3$  below the Néel temperature. Here we highlight the actual evaluation of the matrix elements relevant for the nonreciprocal nonlinear susceptibilities. The evaluation of the matrix elements is performed within a cluster model for  $\text{Cr}_2\text{O}_3$ , which contains the full crystal symmetry of  $\text{Cr}_2\text{O}_3$  and which allows the orders of magnitude of all matrix elements contributing to the nonreciprocal phenomena in  $\text{Cr}_2\text{O}_3$  to be predicted. We apply the microscopic model to the observed phenomenon of SHG (Ref. 7) and explain how antiferromagnetic domains can be distinguished experimentally. We also apply our model to another nonreciprocal effect seen experimentally in  $\text{Cr}_2\text{O}_3$  viz., gyrotropic birefringence<sup>6</sup> and solve the long-standing question regarding its magnitude. Our model can also be used to describe nonreciprocal optical effects in other antiferromagnets where inversion symmetry is broken below  $T_N$ .

The paper is organized as follows. In Sec. II, we illustrate how symmetry arguments can be used to study nonreciprocal effects by considering the macroscopic theory of SHG in  $\text{Cr}_2\text{O}_3$ . In Sec. III, we present the microscopic theory of SHG which allows us to obtain all polarization selection rules and magnitudes of the nonlinear susceptibilities. In Sec. IV, we use our microscopic model to explain the phenomenon of gyrotropic birefringence and the associated magne-

toelectric effect. A summary of our results and conclusions are presented in Sec. V.

## II. MACROSCOPIC THEORY

A clue to the origin of nonreciprocal effects can be obtained from macroscopic (symmetry) considerations of the susceptibility tensors. The optical properties of a medium are characterized by linear and nonlinear susceptibility tensors. If the susceptibility tensors are known for a given medium up to a certain order  $n$ , then, at least in principle, the  $n$ th-order nonlinear optical effects in the medium can be predicted from Maxwell's equations. Physically, the susceptibility is related to the microscopic structure of the medium and can be properly evaluated only by doing a full quantum-mechanical calculation as we will show in the next section. Nevertheless, one can get some information about the susceptibilities just from symmetry considerations as dictated by Neumann's principle, which states<sup>11</sup> that any symmetry which is exhibited by the point group of the crystal is possessed by every physical property of the crystal. Then, to investigate the effect of crystal symmetry on the components of the susceptibility tensors, it is necessary to enforce the requirement that the tensor be invariant under all the permissible symmetry operators appropriate to the particular crystal class. Accordingly, some tensor elements are zero or are related to others, thereby reducing the total number of independent tensor elements. The application of Neumann's principle to four-dimensional space time remains valid only for static properties. For dynamic processes, like nonreciprocal SHG, where there is a preferred direction of time, one considers only those symmetry operations that do not include time reversal in classifying the allowed tensors, i.e., only the spatial symmetry is used to simplify the form of the susceptibility tensors. Though one can still classify the tensors as  $i$  and  $c$  (time-symmetric/antisymmetric) tensors, one cannot use this classification to obtain those that are allowed. To illustrate these notions, let us now consider the macroscopic theory of SHG in  $\text{Cr}_2\text{O}_3$ .<sup>7</sup> We shall consider in detail the case where the spins are oriented parallel to the crystallographic  $z$  axis and laser light propagates along the  $z$  direction and then we shall generalize to the case of arbitrary direction for the orientation of the spins and for the propagation of the laser light.

### A. Spins and laser light parallel to the $z$ axis

Above the Néel temperature,  $T_N \approx 307$  K,  $\text{Cr}_2\text{O}_3$  crystallizes in the centrosymmetric point group  $D_{3d}$ . The four  $\text{Cr}^{3+}$  ions in the unit cell occupy equivalent  $c$  positions along the  $3_z$  (optic) axis. Since this structure has a center of inversion, parity considerations forbid electric dipole transitions in SHG. Magnetic dipole transitions that are related to the existence of an axial tensor of odd rank, or electric quadrupole transitions related to the existence of a polar tensor of even rank are however allowed. Below  $T_N$ , the spins of the  $\text{Cr}^{3+}$  ions orient along the  $z$  axis. The spin ordering breaks time-reversal symmetry  $R$  and as SHG is a dynamic process, only symmetry operations of the crystal that do not include  $R$  may be used to classify the allowed tensors for the susceptibilities. For  $\text{Cr}_2\text{O}_3$ , the remaining invariant subgroup is

$D_3$ . New tensors are allowed in this point group, for instance, a polar tensor of odd rank, that allow electric dipole transitions in SHG.

From Maxwell's equations, the source term corresponding to SHG can be derived by considering the contributions to (nonlinear) magnetization,  $\mathbf{M}^{(2\omega)} = \epsilon_0 c \gamma^{(2\omega)} : \mathbf{E}^{(\omega)} \mathbf{E}^{(\omega)}$  and polarization,  $\mathbf{P}^{(2\omega)} = \epsilon_0 \chi^{(2\omega)} : \mathbf{E}^{(\omega)} \mathbf{E}^{(\omega)}$ , in the point group  $D_3$ . In general, one should also consider contributions to nonlinear susceptibilities related to electric quadrupole transitions, viz.,  $\mathbf{Q}^{(2\omega)} = (-ic \epsilon_0 / 2\omega) \tilde{\chi}^{(2\omega)} : \mathbf{E}^{(\omega)} \mathbf{E}^{(\omega)}$ . Since the basic physics associated with such transitions is not different from the magnetic dipole transitions, we will in the following concentrate on the electric and magnetic dipole contributions to the nonlinear susceptibilities. If we assume that laser light propagates along the optic axis, there is only one independent component  $\gamma_m \equiv \gamma_{yyy} = -\gamma_{yxx} = -\gamma_{xyx} = -\gamma_{xxy}$  of the nonlinear magnetic susceptibility (axial tensor of third rank) and analogously for the nonlinear electric susceptibility (polar tensor of third rank),  $\chi_e \equiv \chi_{yyy} = -\chi_{yxx} = -\chi_{xyx} = -\chi_{xxy}$ . The source term  $\mathbf{S}(\mathbf{r}, t)$  in the wave equation,

$$[\nabla \times (\nabla \times) + (1/c^2) \partial^2 / \partial t^2] \mathbf{E}(\mathbf{r}, t) = -\mathbf{S}(\mathbf{r}, t), \quad (1)$$

can be written in a dipole expansion as<sup>12</sup>

$$\mathbf{S}(\mathbf{r}, t) = \mu_0 \left( \frac{\partial^2 \mathbf{P}(\mathbf{r}, t)}{\partial t^2} + \nabla \times \frac{\partial \mathbf{M}(\mathbf{r}, t)}{\partial t} - \nabla \frac{\partial^2 \mathbf{Q}(\mathbf{r}, t)}{\partial t^2} + \dots \right). \quad (2)$$

If we now assume that  $\mathbf{E}$ ,  $\mathbf{P}$ , and  $\mathbf{M}$  can be decomposed in a set of plane waves and consider a circular basis with  $\mathbf{E} = E_+ \hat{e}_+ + E_- \hat{e}_- + E_z \hat{e}_z$ , where  $\hat{e}_\pm = (1/\sqrt{2})(\hat{e}_x \pm i\hat{e}_y)$ , one obtains (note the different basis choice with respect to Refs. 7 and 10),

$$\mathbf{S} = \begin{pmatrix} S_+ \\ S_- \\ S_z \end{pmatrix} = \frac{4\sqrt{2}\omega^2}{c^2} \begin{pmatrix} (\gamma_m - i\chi_e) E_-^2 \\ (\gamma_m + i\chi_e) E_+^2 \\ 0 \end{pmatrix}, \quad (3)$$

where  $\hbar\omega$  is the energy of the incoming light beam. Note that incoming right circularly polarized light ( $E_+$ ) leads to left circularly polarized light ( $E_-$ ) and vice versa in SHG. Above  $T_N$ , the electric dipole contributions disappear ( $\chi_e \equiv 0$ ) and therefore the SHG intensities  $I_\pm$  are identical, while below  $T_N$ , ( $\chi_e \neq 0$ ) and the intensities  $I_\pm \propto |\gamma_m \pm i\chi_e|^2 E_\mp^4$  are different for right and left circularly polarized light, as observed experimentally.<sup>7</sup> As the tensor  $\chi$  appears only below  $T_N$ , it is natural to assume that it is proportional to  $\Delta(T)$ , the antiferromagnetic order parameter. Nonreciprocal SHG can then be understood as arising from an interference between  $\gamma_m$  and  $\chi_e$ .

### B. Spins and laser light in arbitrary directions

An extended study of SHG in  $\text{Cr}_2\text{O}_3$  can be carried out by considering the propagation of light and the orientation of the spins in the crystal to be arbitrary, the motivation of such a study being the fact that application of an external magnetic field causes the spins to orient along different directions. The spin-flop phase which occurs in  $\text{Cr}_2\text{O}_3$  when a static magnetic field is applied along the  $z$  direction can be

TABLE I. Predictions for the components of the source term  $\mathbf{S}$  from macroscopic symmetry considerations. A constant term  $4\omega^2/c^2$  has here been omitted for simplicity. The three columns are the predictions for light incident in  $z$ ,  $y$ , and  $x$  directions, respectively. The three rows are for the moment of the  $\text{Cr}^{3+}$  spins aligned parallel to the crystallographic  $z$ ,  $y$ , and  $x$  axis, respectively.  $\gamma_i$  ( $i = m, m_1, m_2, 1$ ) and  $\chi_i$  ( $i = e, e_1, e_2, a, a_1, a_2, b, b_1, b_2, 1, 2, 3, \dots, 10$ ) correspond to the remaining independent components for the magnetic and electric susceptibilities, respectively. See the appendix for an explicit account of these components.

		Direction of incident light		
		$z$	$y$	$x$
$z$	$\begin{pmatrix} \gamma_m(E_x^2 - E_y^2) - 2\chi_e E_x E_y \\ -\chi_e(E_x^2 - E_y^2) - 2\gamma_m E_x E_y \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0 \\ -(\chi_a + \chi_b)E_x E_z - \chi_e E_x E_x \\ 0 \end{pmatrix}$	$\begin{pmatrix} (\chi_a + \chi_b)E_y E_z \\ \chi_e E_y^2 \\ \gamma_m E_y^2 \end{pmatrix}$	
$y$	$\begin{pmatrix} (\chi_3 + \gamma_{m_2})E_x^2 + (\chi_4 - \gamma_{m_1})E_y^2 \\ 2(\chi_4 - \gamma_{m_2})E_x E_y \\ \chi_5 E_x^2 + \chi_6 E_y^2 \end{pmatrix}$	$\begin{pmatrix} \chi_3 E_x^2 + \chi_7 E_z^2 + 2\chi_5 E_x E_z \\ 0 \\ \chi_5 E_x^2 + \chi_8 E_z^2 + 2\chi_7 E_x E_z \end{pmatrix}$	$\begin{pmatrix} \chi_4 E_y^2 + \chi_7 E_z^2 \\ 2(\chi_9 - \gamma_1)E_y E_z \\ (\chi_9 + \gamma_{m_1})E_y^2 + (\chi_8 + \gamma_1)E_z^2 \end{pmatrix}$	
$x$	$\begin{pmatrix} \gamma_{m_2} E_x^2 - \gamma_{m_1} E_y^2 - 2\chi_{e_2} E_x E_y \\ -\chi_{e_2} E_x^2 + \chi_{e_1} E_y^2 - 2\gamma_{m_2} E_x E_y \\ (\chi_{10} + \chi_2)E_x E_y \end{pmatrix}$	$\begin{pmatrix} 0 \\ -\chi_{e_2} E_x^2 + \chi_1 E_z^2 + (\chi_{a_1} + \chi_{b_1})E_x E_z \\ 0 \end{pmatrix}$	$\begin{pmatrix} -(\chi_{a_2} + \chi_{b_2})E_y E_z \\ \chi_{e_1} E_y^2 + \chi_1 E_z^2 - 2\gamma_1 E_y E_z \\ \gamma_{m_1} E_y^2 + \gamma_1 E_z^2 + 2\chi_1 E_y E_z \end{pmatrix}$	

studied using these results. In Table I, we present the results of the macroscopic symmetry analysis below  $T_N$  for light propagating along the  $z$ ,  $y$ , and  $x$  directions and for spins oriented parallel to  $z$ ,  $y$ , and  $x$  axis. The three components of the source term are indicated for the various cases. Note that, in the first row which corresponds to the case that the spins are aligned parallel to the  $z$  axis, the interference effect occurring for light propagating along the  $z$  direction is absent when light propagates along the  $y$  and  $x$  directions, as has been verified experimentally.<sup>13</sup>

When the spins are aligned along the  $z$ ,  $y$ , and  $x$  directions the invariant point subgroups of crystal symmetries are  $D_3$ ,  $C_{1h}$ , and  $C_2$ , respectively. Table I contains the results for the source term components for all three possibilities. Table II contains the components of the source term corresponding to electric quadrupole transitions for light propagating along the  $z$ ,  $y$ , and  $x$  directions and spins aligned parallel to the  $z$  axis.

### III. MICROSCOPIC THEORY OF SECOND HARMONIC GENERATION

The macroscopic theory discussed so far is based purely on symmetry considerations. It can neither provide magni-

tudes of the components of the magnetic ( $\gamma$ ) and electric ( $\chi$ ) susceptibilities nor can it specify the details of the interaction and the origin of the coupling between light and the antiferromagnetic order parameter. Both these can be obtained only from a microscopic approach which is described below. In what follows, we consider in detail the case when the spins are aligned parallel to the  $z$  axis and light propagates along the same direction. This is the most representative case for the observation of nonreciprocal phenomena in  $\text{Cr}_2\text{O}_3$ . Elsewhere, we have shown that nonreciprocal effects can be understood by the fact that electric dipole transitions are allowed below  $T_N$ .<sup>10</sup> We use this in calculating the nonlinear susceptibilities of  $\text{Cr}_2\text{O}_3$ . The method of calculating nonlinear susceptibilities of dielectric media was developed by Armstrong and co-workers.<sup>14</sup> In this approach, the current density induced in the system by incident electromagnetic radiation is calculated using semiclassical perturbation theory.

Let us consider the electromagnetic field to be a superposition of three harmonic waves whose frequencies  $\omega_i$ ,  $i = 1, 2, 3$ , satisfy the condition  $\omega_3 = \omega_1 + \omega_2$ . We choose the vector potential of this field to be

TABLE II. Electric quadrupole contributions to the source term,  $\mathbf{S}$ . The constant  $4\omega^2/c^2$  has been omitted for simplicity. The three columns are the predictions for light incident, in  $z$ ,  $y$ , and  $x$  directions, respectively and for the  $\text{Cr}^{3+}$  spins aligned parallel to the  $z$  axis.  $\tilde{\chi}_i$  ( $i = 1, 2, 3, 4$ ) correspond to the remaining independent components. (See the appendix.)

		Direction of incident light		
		$z$	$y$	$x$
$z$	$\begin{pmatrix} \tilde{\chi}_4(E_x^2 - E_y^2) \\ -2\tilde{\chi}_4 E_x E_y \\ \tilde{\chi}_3(E_x^2 + E_y^2) \end{pmatrix}$	$\begin{pmatrix} 0 \\ \tilde{\chi}_1 E_x^2 + \tilde{\chi}_2 E_z^2 \\ 0 \end{pmatrix}$	$\begin{pmatrix} \tilde{\chi}_2 E_z^2 + \tilde{\chi}_1 E_y^2 \\ -2\tilde{\chi}_4 E_y E_z \\ -\tilde{\chi}_4 E_y^2 \end{pmatrix}$	

$$\mathbf{A}(\mathbf{r}, t) = \sum_i \hat{a}_i q_i \exp(i\mathbf{k} \cdot \mathbf{r} - \omega_i t) + \text{H.c.},$$

where  $\hat{a}_i$  is a unit polarization vector and  $q_i$  determines the strength of the electric field,  $E_i = q_i \omega_i / 2$  (where the Coulomb gauge is being assumed). The perturbation is then described by the usual form of the interaction Hamiltonian

$$H_{\text{int}} = \sum_j \frac{-e}{m_e} \mathbf{A}_j \cdot \mathbf{p}_j + \frac{e^2}{2m_e} \mathbf{A}_j \cdot \mathbf{A}_j.$$

Assuming for simplicity that the ground state wave function  $\Phi$  is a product of one-electron wave functions,  $\Phi = \prod_n \phi_n$ , the induced current density is given in the interaction representation by

$$\sum_n \langle \phi_n | e\mathbf{v} | \phi_n \rangle = \sum_n \langle \phi_n | \mathbf{p} - e\mathbf{A} | \phi_n \rangle \frac{e}{m_e}.$$

Nonlinear susceptibilities are now calculated to the desired order in field strengths. We are, in particular, interested in terms that are quadratic in fields and the source term at  $\omega_3 = \omega_1 + \omega_2$ . Thus we only consider those terms in the perturbation expansion for the current density that are proportional to  $q_1 q_2$ , viz., proportional to  $E_1 E_2$  and with time dependence  $\exp(\pm i\omega_3 t)$  and write

$$\begin{aligned} \langle e\mathbf{v}(\omega_3) \rangle &= \langle e\mathbf{v}^{(+)}(\omega_3) \exp(i\omega_3 t) \rangle \\ &\quad + \langle e\mathbf{v}^{(-)}(\omega_3) \exp(-i\omega_3 t) \rangle. \end{aligned}$$

By multiplying the terms proportional to  $\exp(\pm i\omega_3 t)$  by

$\exp(\mp i\mathbf{k}_3 \cdot \mathbf{r})$  and then taking the expectation value, we get the induced current density corresponding to the source term at  $\omega_3$  and at  $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3$  as

$$\langle \mathbf{J}(\mathbf{k}_3, \omega_3) \rangle = \langle \Phi | e\mathbf{v}^{(-)}(\omega_3) \exp(i\mathbf{k}_3 \cdot \mathbf{r} - \omega_3 t) | \Phi \rangle. \quad (4)$$

One can now obtain the expression for the nonlinear susceptibilities by using the relation  $\mathbf{J} = \mu_0 \partial \mathbf{P} / \partial t$  as also the defining relations for the susceptibilities that relate, for example,  $\mathbf{P}$  and  $\mathbf{E}$ .

We now turn our attention to the specific case of  $\text{Cr}_2\text{O}_3$ . As explained in the previous section, we are interested in the nonlinear polarization  $\mathbf{P}^{(2\omega)}$  and the magnetization  $\mathbf{M}^{(2\omega)}$ . The nonlinear susceptibility  $\chi$  is only allowed below the Néel temperature where spatial inversion symmetry of the crystal is broken by antiferromagnetic ordering. In an earlier paper,<sup>10</sup> we have shown that this leads to electric dipole transitions between the  ${}^4A_2$  and  ${}^4T_2$  levels of  $\text{Cr}_2\text{O}_3$ . Thus, below  $T_N$ , one can use the electric dipole approximation with the interaction Hamiltonian of the form

$$H = -e \sum_i \mathbf{E}_i \cdot \mathbf{r}.$$

A simple calculation now yields the result for the induced current,

$$\begin{aligned} \langle \mathbf{J}(\mathbf{k}_3, \omega_3) \rangle &= \frac{e^2}{2\hbar^2} \sum_{|m\rangle, |n\rangle} \left[ \frac{\langle \Phi | \mathbf{J}(\mathbf{k}_3, \omega_3) | m \rangle \langle m | E_\mu r_\mu | n \rangle \langle n | E_\nu r_\nu | \Phi \rangle}{(\omega_m - 2\omega)(\omega_n - \omega)} + \frac{\langle \Phi | E_\mu r_\mu | m \rangle \langle m | \mathbf{J}(\mathbf{k}_3, \omega_3) | n \rangle \langle n | E_\nu r_\nu | \Phi \rangle}{(\omega_m + \omega)(\omega_n - \omega)} \right. \\ &\quad \left. + \frac{\langle \Phi | E_\mu r_\mu | m \rangle \langle m | E_\nu r_\nu | n \rangle \langle n | \mathbf{J}(\mathbf{k}_3, \omega_3) | \Phi \rangle}{(\omega_n + 2\omega)(\omega_m + \omega)} \right], \end{aligned} \quad (5)$$

where  $E_\mu$  are the components of the incident electric fields and definition (4) is to be used. In the above expression we have also taken (as in SHG)  $\omega_1 = \omega_2 = \omega$  and  $\omega_3 = 2\omega$ . All factors  $\exp(i\mathbf{k} \cdot \mathbf{r})$  have been set to unity (electric dipole approximation). The problem now reduces to that of evaluating the appropriate transition matrix elements in the above expression with the  $\text{Cr}^{3+}$  wave functions. To do this, we consider a cluster model that has the correct symmetry of  $\text{Cr}_2\text{O}_3$ , viz.,  $D_{3d}$ . This model<sup>10</sup> contains only two Cr ions in a magnetic unit cell whereas in the actual structure of  $\text{Cr}_2\text{O}_3$  there are four. While this would lead to quantitative differences, the basic physics remains the same.

The ground-state wave function of the magnetic ion can be written as  $^{10}|\Phi\rangle = |t_2^{(1)}, t_2^{(2)}, t_2^{(3)}\rangle$  and the excited states  $|e\rangle = |e^{(1)}\rangle, |e^{(2)}\rangle$ , where

$$t_2^{(1)} = -|d_{3z^2-r^2}\rangle + \eta_1 |p_z\rangle,$$

$$t_2^{(2)} = 3^{-1/2} [\sqrt{2}|d_{x^2-y^2}\rangle + |d_{zx}\rangle] + \eta_2 |p_x\rangle,$$

$$t_2^{(3)} = -3^{-1/2} [\sqrt{2}|d_{xy}\rangle + |d_{yz}\rangle] + \eta_2 |p_y\rangle, \quad (6)$$

$$e^{(1)} = 3^{-1/2} [|d_{xy}\rangle - \sqrt{2}|d_{yz}\rangle] + \eta_3 |p_y\rangle,$$

$$e^{(2)} = 3^{-1/2} [|d_{x^2-y^2}\rangle + \sqrt{2}|d_{zx}\rangle] + \eta_3 |p_x\rangle,$$

Here the  $|d\rangle$  and  $|p\rangle$  states are the Cr 3d and Cr 4p orbitals, respectively. In deriving the above wave functions, we have

chosen the axis of quantization to be parallel to the crystallographic  $z$  direction. The following convention for the  $d$  orbitals is chosen:

$$\begin{aligned} d_{xy} &= -\frac{R(r)}{r^2} \left( \frac{15}{4\pi} \right)^{1/2} xy, \\ d_{yz} &= \frac{R(r)}{r^2} \left( \frac{15}{4\pi} \right)^{1/2} yz, \\ d_{zx} &= -\frac{R(r)}{r^2} \left( \frac{15}{4\pi} \right)^{1/2} xz, \\ d_{x^2-y^2} &= \frac{R(r)}{r^2} \left( \frac{15}{16\pi} \right)^{1/2} (x^2-y^2), \\ d_{3z^2-r^2} &= \frac{R(r)}{r^2} \left( \frac{5}{16\pi} \right)^{1/2} (3z^2-r^2). \end{aligned}$$

Here the  $R(r)$  are the appropriate radial functions for  $3d$  orbitals. Spin quantum numbers in (6) have been suppressed for clarity. We also note that the expression (6) only includes the effect of the hemihedral part of the trigonal distortion which is the most dominant interaction. This interaction is of the form  $\eta z$  and leads to a mixing of Cr  $3d$  states and Cr  $4p$  states ( $p_x, p_y, p_z$ ) with coefficients  $\eta_1, \eta_2$ , and  $\eta_3$  being proportional to  $\eta$ , the trigonal field. In addition to this mixing, the spin-orbit coupling also causes a mixing of the  $t_2$  and  $e$  orbitals. As explained in our previous paper, it is this interplay between the trigonal distortion and the spin-orbit coupling that leads to electric dipole transitions below  $T_N$ . Consequently, we focus our attention on those transition matrix elements in (5) that are proportional to *both* the spin-orbit interaction and the trigonal field. It is easy to see that such matrix elements are of the form

$$\langle t_2 | L_z S_z | e \rangle \langle e | \mathbf{r} | m \rangle \langle m | E_\mu r_\mu | n \rangle \langle n | E_\nu r_\nu | t_2 \rangle, \quad (7)$$

where we have used  $\langle m | \mathbf{p} | n \rangle = -im_e(\omega_n - \omega_m) \langle m | \mathbf{r} | n \rangle$ , etc. Let us now consider the case when the incident light is right circularly polarized,<sup>7</sup> viz.,  $\mathbf{E} = E \hat{e}_+$  where  $\hat{e}_\pm = 1/\sqrt{2}(\hat{e}_x \pm i\hat{e}_y)$ . The relevant transition matrix element is now given by

$$\sum_{\substack{i=2,3 \\ j=1,2}} \langle t_2^{(i)} | L_z S_z | e^{(j)} \rangle \langle e^{(j)} | \mathbf{r} | e^{(j)} \rangle \langle e^{(j)} | r_+ | n \rangle \langle n | r_+ | t_2^{(i)} \rangle,$$

where the states  $|n\rangle$  are higher-energy orbitals of odd symmetry. Let us now consider that part of the transition matrix element given above which corresponds to the emission of the second harmonic, viz.,

$$\langle t_2^{(i)} | L_z S_z | e^{(j)} \rangle \langle e^{(j)} | \mathbf{r} | e^{(j)} \rangle.$$

Since the excited state Cr orbital  $|e^{(j)}\rangle$  is a mixture of the Cr  $3d$  and  $4p$  states, the emission matrix element has contributions of the form

$$\eta \langle t_2^{(i)} | L_z S_z | e^{(j)} \rangle \langle p^{(j)} | \mathbf{r} | e^{(j)} \rangle, \quad (8)$$

where  $\eta$  is the appropriate admixture of the  $p$  and  $d$  orbitals determined by (6). Equation (8) describes the contribution to

the electric dipole (ED) matrix element of a single Cr ion. The response of the crystal is given by the coherent summation over the contributions of each ion. In  $\text{Cr}_2\text{O}_3$  there are two pairs of sites in the unit cell, the  $A/B$  and the  $A'/B'$  sites related by inversion symmetry. Since they give identical contributions we need to consider only one of the pairs. The contribution of a given unit cell to the ED matrix element is then proportional to

$$\lambda (\eta_A \langle S_z \rangle_A + \eta_B \langle S_z \rangle_B), \quad (9)$$

where  $\lambda$  is the spin-orbit coupling constant (see Ref. 10) and  $\eta_A$  and  $\eta_B$  are proportional to the respective local trigonal fields. Inversion symmetry demands that  $-\eta_B = \eta_A \equiv \eta$ .<sup>15</sup> The total contribution to the ED matrix element is then proportional to

$$\sum_{\text{all unit cells}} \lambda \eta (\langle S_z \rangle_A - \langle S_z \rangle_B) \text{const} \equiv \lambda \eta \Delta(T),$$

where  $\Delta(T)$  is the antiferromagnetic order parameter. One can use the explicit form of the orbitals given by (6) and evaluate the desired matrix elements. For example, the contribution to SHG by exciting the electron in the orbital  $t_2^{(2)}$  is proportional to

$$\begin{aligned} \lambda \eta \Delta(T) [ &\langle d_{(x^2-y^2)} | L_z | d_{xy} \rangle \langle d_{xy} | x | p_y \rangle \langle p_y | z | d_{yz} \rangle \\ &\times \langle d_{yz} | (\mathbf{E} \cdot \mathbf{r})^2 | d_{zx} \rangle ]. \end{aligned}$$

A similar expression can be written for the contribution arising from  $t_2^{(3)}$ . From our results we find that (a) the  $t_2^{(1)}$  orbital does not contribute to SHG. This is not surprising as our mechanism of SHG is mediated through the diagonal part of the spin-orbit interaction and  $L_z t_2^{(1)} = 0$ . (b) The electric field of the emitted radiation at frequency  $2\omega$  is along the  $\hat{x} - i\hat{y}$  direction, i.e., incoming right circularly polarized light generates the second harmonic with opposite polarization. Likewise, it can be verified that left circularly polarized light generates a second harmonic that is right circularly polarized. Thus our microscopic results reproduce the selection rules that are given by macroscopic theory. This is because the expression (6) for the  $\text{Cr}^{3+}$  orbitals has been obtained by incorporating the full crystal symmetry of  $\text{Cr}_2\text{O}_3$ .

The constructive interference in emission of the contributions to the ED matrix elements below  $T_N$ , as given by Eq. (9), is a consequence of the symmetry of the spin ordering in  $\text{Cr}_2\text{O}_3$ . We reemphasize that this is because our mechanism is a one-ion mechanism that invokes the *diagonal* part of the spin-orbit interaction. Photons absorbed by a certain ion are, in this mechanism, reemitted by the same ion. The phase of the emitted electromagnetic wave then depends on the relative direction of the spin-ordering with respect to the direction of the trigonal distortion at the given site (9). The coherent interference of the waves emitted by all ions may then interfere constructively. The effect is nonreciprocal since the direction of the local trigonal distortion is invariant under time reversal, whereas the spin order is not.

Let us now consider the case  $T > T_N$ . Now, inversion is a good symmetry of the crystal and the electric dipole transitions vanish identically. In this case, one has to consider the

nonvanishing term of the lowest order in the multipole expansion of  $\exp(-i\mathbf{k}_3 \cdot \mathbf{r})$ . This is, of course, the magnetic dipole term which can be written as

$$\begin{aligned} \langle \mathbf{J}(\mathbf{k}_3, \omega_3) \rangle &= \frac{ie^3 k_3}{4m_e^3 \hbar^2} q_1 q_2 \sum_{|m\rangle, |n\rangle} \langle \Phi | \mathbf{L} | m \rangle \langle m | \exp(-i\mathbf{k}_1 \cdot \mathbf{r}) a_{1\mu} p_\mu | n \rangle \langle n | \exp(-i\mathbf{k}_2 \cdot \mathbf{r}) a_{2\nu} p_\nu | \Phi \rangle \\ &\times \frac{\exp(i\omega_3 t)}{(\omega_m - \omega_n + \omega_1)(\omega_n + \omega_2)} + \dots \end{aligned} \quad (10)$$

The calculation of transition matrix elements in this case is much simpler as now the dominant contributions contain neither the spin-orbit interaction nor the trigonal distortion. It is easy to verify that one only has to consider contributions to the transition matrix elements that are of the form

$$\sum_{i=1,2,3} \sum_{j=1,2} \langle t_2^{(i)} | \mathbf{L} | e^{(j)} \rangle \langle e^{(j)} | r_+ | n \rangle \langle n | r_+ | t_2^{(i)} \rangle, \quad (11)$$

at any given Cr site. (Here again we have assumed that the incoming light is right circularly polarized.) The contributions from different sites can be added up coherently. As in the previous case of the ED transition, we have also verified using (6) that the correct polarization selection rules are reproduced by the above expression below and above  $T_N$ .

The microscopic expression for the dynamical current operator together with the Cr ion wave functions (6) enables us to estimate the magnitudes of the nonlinear susceptibilities. Since we do not have the correct wave functions of the excited states, our estimates are approximate, correct only to an order of magnitude. In particular one may also include contributions from the O  $2p$  orbitals in (6). Such a contribution would not alter the mechanism for the ED transition explained above but would lead to certain quantitative corrections. From expressions (2) and (5), as also the definition of the macroscopic susceptibility  $\chi$  we obtain the order of magnitude of  $\chi^{(2\omega)}$  as approximately

$$|\chi^{(2\omega)}| \approx \frac{8n_0 e^3}{\epsilon_0} \left( \frac{a_0}{2\hbar\omega} \right)^2 \frac{\lambda_0}{a_0} \frac{\hbar}{mc} \frac{\lambda}{E_e - E_{t_2}} \frac{\eta}{E_p - E_d} \Delta(T). \quad (12)$$

Here,  $\lambda_0 \approx 5000 \text{ \AA}$  is the wavelength of the emitted light,  $a_0 \approx 0.69 \text{ \AA}$  is the radius of  $\text{Cr}^{3+}$ ,  $n_0$  is the density of Cr ions in  $\text{Cr}_2\text{O}_3$  ( $\approx 3.3 \times 10^{28} \text{ m}^{-3}$ ),  $\lambda \approx 100 \text{ cm}^{-1}$  is the spin-orbit interaction,<sup>16,17</sup>  $E_e - E_{t_2} \approx 8000 \text{ cm}^{-1}$  is the difference in energy between the  $t_2$  and the  $e$  orbitals,  $\eta \approx 350 \text{ cm}^{-1}$  is the trigonal field,<sup>17</sup>  $E_p - E_d \approx 8 \times 10^4 \text{ cm}^{-1}$  is the difference in energy between the  $d$  and the  $p$  orbitals that are mixed by the trigonal distortion and  $\Delta(T)$  is the antiferromagnetic order parameter. The temperature dependence of  $\chi$  is solely through that of the antiferromagnetic order parameter and consequently  $\chi$  vanishes above  $T_N$ . At temperatures much lower than  $T_N$  we find that  $|\chi^{(2\omega)}| \approx 8.7 \times 10^{-16} \text{ C N}^{-1}$ .

Similarly, we find that the magnitude of  $\gamma^{(2\omega)}$  is approximately

$$|\gamma^{(2\omega)}| \approx \frac{4n_0 e^3}{\epsilon_0} \left( \frac{a_0}{2\hbar\omega} \right)^2 \frac{\hbar}{4mc}. \quad (13)$$

As explained earlier, this is the magnetic dipole (MD) contribution to SHG which depends neither on the trigonal distortion nor the spin-orbit interaction. It is also independent of temperature and we estimate it to be of the order of  $11 \times 10^{-16} \text{ C N}^{-1}$ . The contributions to  $\mathbf{J}$  from the nonlinear susceptibilities  $\chi$  and  $\gamma$  can produce interference effects in SHG only if the first two terms in the right-hand side of equation (2) are of the same order of magnitude, viz.,  $|\chi| \approx |\gamma|$ . From our estimates of  $\chi$  and  $\gamma$  above we find that this is indeed satisfied thereby leading to an interference effect in SHG which is nonreciprocal and which vanishes above  $T_N$ .

#### IV. GYROTROPIC BIREFRINGENCE AND THE OPTICAL MAGNETOELECTRIC EFFECT

The ED transition in the optical region that is allowed below  $T_N$  in  $\text{Cr}_2\text{O}_3$  can also be seen in one-photon experiments. In this section, we consider the phenomena of gyrotropic birefringence (GB) and the associated optical magnetoelectric effect that are one-photon processes in contrast to SHG which is a two-photon process.

GB is a nonreciprocal optical effect that appears as a shift in the principal optical axis along with a change in the velocity of propagation of light. The possibility of observing this effect in  $\text{Cr}_2\text{O}_3$  and using it to distinguish between antiferromagnetic domains was first pointed out by Brown and co-workers.<sup>4</sup> Their analysis of the problem was purely macroscopic and they showed that GB appears in the form of a polar  $c$  tensor (one that changes sign under both space and time inversion) below  $T_N$ . Later, Hornreich and Shtrikman<sup>18</sup> presented the first quantum-mechanical treatment of this problem. They showed that the gyrotropic birefringence tensor can be described in terms of electric quadrupole and magnetoelectric effects. From their results, they estimated that at optical frequencies, the induced rotation of the principal optical axes of  $\text{Cr}_2\text{O}_3$  would be of the order of  $10^{-8} - 10^{-6}$  rad and the magnetoelectric susceptibility would be of the order of  $10^{-8}$  (in dimensionless units). This phenomenon was also analyzed by Graham and Raab<sup>19</sup> using a multipole theory of wave propagation.

Recently however, Krichetsov *et al.*<sup>6</sup> observed spontaneous nonreciprocal rotation of the optical axes in  $\text{Cr}_2\text{O}_3$ .

They found that the observed rotation and the magnetoelectric susceptibility were four orders of magnitude larger than those predicted by Hornreich and Shtrikman. They also found that the observed temperature dependence of these nonreciprocal effects corresponds roughly to that of the antiferromagnetic order parameter, something that does not follow obviously from previous calculations.<sup>18</sup> The intensity of these effects and the temperature dependence led them to speculate that these effects were attributable to ED transitions in the optical range. We now show that this is indeed the case and the mechanism we discussed earlier does lead to effects that are of the same order of magnitude as those observed.

To see this, we calculate the magnetoelectric susceptibility in the optical region, allowing for an ED transition below  $T_N$ . The calculation is in many ways similar to that presented earlier for the nonlinear susceptibilities. The magnetoelectric susceptibility is defined as  $\mathbf{M}^{(\omega)} = \alpha: \mathbf{E}^{(\omega)}$  and we estimate it by calculating directly, the quantity  $\langle \mathbf{M} \rangle = g \mu_B \langle \mathbf{L} + 2\mathbf{S} \rangle$  in perturbation theory. Since in this case we are only interested in temperatures below the Néel temperature, we use the electric dipole approximation and consider the linear response of the system. It is easy to verify that the induced magnetization is given by

$$\langle \mathbf{M} \rangle = \frac{e}{\hbar} \text{Re} \left[ \sum_{|m\rangle} \langle \Phi | \mathbf{M} | m \rangle \frac{\langle m | \mathbf{E} \cdot \mathbf{r} | \Phi \rangle}{(\omega - \omega_m)} \exp(-i\omega t) + \langle \Phi | \mathbf{M} | m \rangle \frac{\langle m | \mathbf{E} \cdot \mathbf{r} | \Phi \rangle}{(\omega + \omega_m)} \exp(+i\omega t) \right],$$

where we have assumed the electric field to be of the form  $\mathbf{E} = \mathbf{E}_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t)$ . Choosing (as in the experiment<sup>6</sup>) the incident light along the  $\hat{x}$  direction and the electric field  $\mathbf{E} \parallel \hat{z}$ , it is easy to see that a typical matrix element that would contribute to the magnetoelectric susceptibility is of the form,

$$\langle t_2 | L_z | e \rangle \langle e | L_z S_z | t_2 \rangle \langle t_2 | z E_z | t_2 \rangle.$$

Note that  $\langle t_2 | z E_z | t_2 \rangle$  would be proportional to the trigonal mixing of the  $3d$  and the  $4p$  orbitals. A straightforward calculation using (6) to evaluate appropriate transition matrix elements gives us the expression for the magnetoelectric susceptibility,

$$\alpha_{xx} \sim 4 \mu_0 c e \frac{g \mu_B}{\hbar(\omega - \omega_m)} \frac{\lambda}{E_e - E_{t_2}} \frac{\eta}{E_p - E_d} n_0 \Delta(T), \quad (14)$$

in dimensionless units. Here,  $n_0$  is the density of Cr ions in  $\text{Cr}_2\text{O}_3$  ( $\approx 3.3 \times 10^{28} \text{ m}^{-3}$ ) and  $\hbar(\omega - \omega_m) \sim 0.5 \text{ eV}$  in the region of experimental interest. Thus by evaluating the above expression, we estimate  $\alpha_{xx} \sim 0.2 \times 10^{-4}$  which is of the same order of magnitude as that observed experimentally. This also means that the nonreciprocal rotation would be  $\sim 10^{-4}$  rad. Since the ED process that we consider couples light to the order parameter, the observed temperature dependence follows naturally from our theory.

## V. SUMMARY AND CONCLUSIONS

In this paper we have developed a microscopic theory of nonreciprocal optical effects observed below  $T_N$  in  $\text{Cr}_2\text{O}_3$ . We have shown that these effects can be explained by an electric dipole process that arises from an interplay between the spin-orbit coupling and the trigonal distortion of the ligand field. Such a process couples light directly to the antiferromagnetic order parameter. In contrast to other ED mechanisms that have been considered in the literature so far,<sup>20</sup> our mechanism is a one-ion mechanism that couples light to the sublattice magnetization rather than any magnetic excitations. Photons absorbed by a certain  $\text{Cr}^{3+}$  ion are also emitted by the same ion. The coupling to the antiferromagnetic order parameter then occurs through constructive interference of the photons emitted by different Cr ions.

It might seem that our mechanism leads to effects that are weak as they involve the trigonal distortion and spin-orbit interaction, both weak effects by themselves. However their interplay leads to an electric dipole transition whose oscillator strength is large in the optical region. Consequently, observed effects are strong. Though we have used this mechanism to explain successfully the phenomena of second-harmonic generation, gyrotropic birefringence, and the optical magnetoelectric effect that have been observed experimentally in  $\text{Cr}_2\text{O}_3$ , our theory can be generalized to all materials where (i) the magnetic ion is not at a center of inversion and (ii) inversion is still a macroscopic symmetry above  $T_N$  but is broken below  $T_N$  due to the ordering of the magnetic ions. Thus, nonreciprocal effects should be observable, for example, in the cuprate  $\text{Gd}_2\text{CuO}_4$  below the ordering temperature of the gadolinium magnetic subsystem,  $T_N(\text{Gd}) = 6.5 \text{ K}$ ,<sup>21</sup> when inversion symmetry is broken as also in  $\text{V}_2\text{O}_3$  and  $\text{MnTiO}_3$ .

## ACKNOWLEDGMENTS

We acknowledge several discussions with T. Djelani, M. Fiebig, D. Fröhlich, G. Sluyterman v. L., and H. J. Thiele. This work was supported by the Deutsche Forschungsgemeinschaft, the Graduiertenkolleg ‘‘Festkörperspektroskopie’’ and by the European Community Human Capital and Mobility program.

## APPENDIX

The components for the nonlinear susceptibilities ( $\chi$ ) and ( $\gamma$ ) in Table I are as follows:

$$\chi_e \equiv \chi_{yy} = -\chi_{yx} = -\chi_{xy} = -\chi_{xy},$$

$$\chi_{e1} \equiv \chi_{yy},$$

$$\chi_{e2} \equiv -\chi_{yx} = -\chi_{xy} = -\chi_{xy},$$

$$\chi_a \equiv \chi_{yxz} = -\chi_{xyz},$$

$$\chi_{a1} \equiv \chi_{yxz},$$

$$\chi_{a2} \equiv -\chi_{xyz},$$

$$\chi_b \equiv \chi_{yzx} = -\chi_{xzy},$$

$$\chi_{b_1} \equiv \chi_{yzx},$$

$$\chi_{b_2} \equiv -\chi_{xzy},$$

$$\chi_1 \equiv \chi_{zzy} = \chi_{zyz} = \chi_{yzz},$$

$$\chi_2 \equiv \chi_{zyx},$$

$$\chi_3 \equiv \chi_{xxx},$$

$$\chi_4 \equiv \chi_{xyy} = \chi_{yyx} = \chi_{yxy},$$

$$\chi_5 \equiv \chi_{zxx} = \chi_{xxz} = \chi_{xzx},$$

$$\chi_6 \equiv \chi_{zyy} = \chi_{yzy} = \chi_{yyz},$$

$$\chi_7 \equiv \chi_{zxx} = \chi_{zxx} = \chi_{xzz},$$

$$\chi_8 \equiv \chi_{zzz},$$

$$\chi_9 \equiv \chi_{yyz} = \chi_{yzy} = \chi_{zyy},$$

$$\chi_{10} \equiv \chi_{zxy},$$

$$\gamma_m \equiv \gamma_{yyy} = -\gamma_{yxx} = -\gamma_{xyx} = -\gamma_{xyx},$$

$$\gamma_{m_1} \equiv \gamma_{yyy},$$

$$\gamma_{m_2} \equiv -\gamma_{xxy} = -\gamma_{xyx} = -\gamma_{yxx},$$

$$\gamma_1 \equiv \gamma_{zzy} = \gamma_{zyz} = \gamma_{yzz}.$$

Above the Néel temperature all  $\chi$ 's and  $\gamma_1$  vanish (and  $\gamma_{m_1} = \gamma_{m_2} \equiv \gamma_m$ ). It is then reasonable to assume that below  $T_N$   $\gamma_1$  is much smaller than all other matrix elements since it is of magnetic dipole character and only allowed due to the breaking of inversion symmetry below the Néel temperature. The components of the electric quadrupole susceptibilities in Table II are as follows:

$$\tilde{\chi}_1 \equiv \tilde{\chi}_{xxyy} = \tilde{\chi}_{yyxx},$$

$$\tilde{\chi}_2 \equiv \tilde{\chi}_{xxzz} = \tilde{\chi}_{yyzz},$$

$$\tilde{\chi}_3 \equiv \tilde{\chi}_{zxxz} = \tilde{\chi}_{zzyy},$$

$$\begin{aligned} \tilde{\chi}_4 \equiv & -\tilde{\chi}_{zxyy} = \tilde{\chi}_{zxxx} = -\tilde{\chi}_{zyxy} = -\tilde{\chi}_{zyyx} = -\tilde{\chi}_{xyzy} \\ & = -\tilde{\chi}_{xyyz} = -\tilde{\chi}_{xzzy}. \end{aligned}$$

- 
- <sup>1</sup>For a discussion of reciprocity in optics, see A. L. Shelankov and G. E. Pinkus, *Phys. Rev. B* **46**, 3326 (1992).
- <sup>2</sup>P. N. Argyres, *Phys. Rev.* **97**, 334 (1955).
- <sup>3</sup>I. E. Dzyaloshinskii, *Zh. Éksp. Teor. Fiz.* **37**, 881 (1959) [*Sov. Phys. JETP* **10**, 628 (1960)].
- <sup>4</sup>W. F. Brown, Jr., S. Shtrikman, and D. Treves, *J. Appl. Phys.* **34**, 1233 (1963).
- <sup>5</sup>R. A. Fleury and R. Loudon, *Phys. Rev.* **166**, 514 (1968). For a comprehensive review, see M. G. Cottam and D. J. Lockwood, *Light Scattering in Magnetic Solids* (Wiley-Interscience, New York, 1986).
- <sup>6</sup>B. B. Krichevstov, V. V. Pavlov, R. V. Pisarev, and V. N. Gridnev, *J. Phys. Condens. Matter* **5**, 8233 (1993).
- <sup>7</sup>M. Fiebig, D. Fröhlich, B. B. Krichevstov, and R. V. Pisarev, *Phys. Rev. Lett.* **73**, 2127 (1994).
- <sup>8</sup>M. Fiebig, D. Fröhlich, and G. Sluyterman v. L., *Appl. Phys. Lett.* **66**, 2906 (1995).
- <sup>9</sup>Note, however, that domain walls can be observed optically in certain antiferromagnets when they are associated with crystal distortions. See W. L. Roth, *J. Appl. Phys.* **31**, 2000 (1960).
- <sup>10</sup>V. N. Muthukumar, R. Valentí, and C. Gros, *Phys. Rev. Lett.* **75**, 2766 (1995).
- <sup>11</sup>R. R. Birss, *Symmetry and Magnetism* (North-Holland, Amsterdam, 1964).
- <sup>12</sup>L. Rosenfeld, *Theory of Electrons* (Interscience, New York, 1951).
- <sup>13</sup>M. Fiebig, H. J. Thiele, and D. Fröhlich (private communication).
- <sup>14</sup>J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, *Phys. Rev.* **127**, 1918 (1962).
- <sup>15</sup>Y. Tanabe, *Prog. Theor. Phys. Suppl.* **14**, 17 (1960); S. Sugano, *ibid.* **14**, 66 (1960); T. Izuyama and G. W. Pratt, Jr., *J. Appl. Phys.* **34**, 1226 (1963).
- <sup>16</sup>G. T. Rado, *Phys. Rev. Lett.* **6**, 609 (1961).
- <sup>17</sup>S. Sugano and Y. Tanabe, *J. Phys. Soc. Jpn.* **13**, 880 (1958).
- <sup>18</sup>R. M. Hornreich and S. Shtrikman, *Phys. Rev.* **171**, 1065 (1968).
- <sup>19</sup>E. B. Graham and R. E. Raab, *J. Phys. Condens. Matter* **6**, 6725 (1994).
- <sup>20</sup>P. A. Fleury and R. Loudon, *Phys. Rev.* **166**, 514 (1968); J. W. Halley and I. Silvera, *Phys. Rev. Lett.* **15**, 656 (1965); see also, Y. Tanabe, R. Moriya, and S. Sugano, *ibid.* **15**, 1023 (1965).
- <sup>21</sup>H. Wiegelmann, A. A. Stepanov, I. M. Vitebsky, A. G. Jansen, and P. Wyder, *Phys. Rev. B* **49**, 10 039 (1994).