Optical phenomena in $BaMnF_4$ near its phase-transition temperatures

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Measurements of indices of refraction, birefringence, and rotation of the optical ellipsoid in $BaMnF_4$ near its incommensurate structural phase-transition temperature and near its two- and three-dimensional magnetic-ordering temperatures have been made. The results are compatible with a single structural phase transition at $T_I=251$ K for the sample used. Small jumps of all measured quantities have been found at T_I that proves the transition to be of first order. The point-group symmetry below T_I is shown to be 2 (C_2) or lower, a result assumed before but never confirmed directly. The optical ellipsoid rotates $\sim 4'$ as temperature is lowered below T_I. Optical activity tensor component $G_{33}=5\times 10^{-5}$ was measured below T_I. Quite unexpectedly the rotation of the optical ellipsoid and the optical activity were found to be temperature independent. Contrary to that, the anomalous part of the index of refraction close to T_I varies with temperature as $\langle(\xi^2+\eta^2)\rangle$ in both phases, where ξ and η are components of the order parameter. In the high-temperature phase $Ama2_1$ (C_{2v}^{12}) close to T_I this varies as $(T-T_I)^{1/2}$ in agreement with theoretical estimations. Fluctuational contributions to the indices of refraction and to the birefringence persist up to ~ 350 K. In the low-temperature phase the order-parameter contribution to the index of refraction is found to vary with the critical exponent $\beta=0.28$. The magnetic contribution to the refractive index at low temperatures is obtained, the highest value being $\delta n_c \simeq 1\times 10^{-3}$.

I. INTRODUCTION

$BaMnF_4$ is a pyroelectric material that displays unusual structural and magnetic phase transitions. Its dynamical and spectroscopic properties have been examined by a variety of techniques recently.[1-6] In the present optical study we have endeavored to clarify several points of interest concerning the incommensurate structural phase transition at $T_I \simeq 250$ K in this material.

(1) Are there any crystal symmetry changes at the transition detectable by optical methods, e.g., by a precise polarimetry?

(2) Is the transition continuous or discontinuous? Two theoretical analyses, both employing renormalization-group techniques, disagree in their predictions.[2,7] Different experiments show the transition to be continuous, but in the study of the birefringence Δn_{ac} the first-order character of the transition was claimed.[6]

(3) What are the critical exponents from optical data both above and below T_I?

(4) What is the width of the fluctuation regime above T_I?

(5) Is there is a second phase transition a few degrees below T_I?

In addition to clarifying some of these problems concerning the structural phase transition, we have performed measurements of the principal refractive indices at low temperatures in order to find two- and three-dimensional magnetic contribution to the optical refraction.

In this study we used two different techniques, namely polarimetric and interferometric techniques. Though both of them are techniques that explore macroscopic properties of crystals (birefringence or refraction), their high sensitivity can supply us with information that is difficult or even impossible to get by other methods. We describe both methods employed in Sec. III of the paper. In Sec. II we present a phenomenological analysis of optical properties of $BaMnF_4$ both above and below T_I. In Sec. IV we give results and their interpretation, and Sec. V concludes the paper.

II. SYMMETRY AND OPTICAL PROPERTIES OF $BaMnF_4$

At room temperature $BaMnF_4$ has orthorhombic crystal structure with the space group $Ama2_1$ (C_{2v}^{12}). The optical indicatrix has the shape of a triaxial ellipsoid with axes along a (x_3), b (x_1), and c (x_2) crystallographic axes. Principal values of the refractive index for $\lambda=589.3$ nm are $n_a=1.499$, $n_b=1.48$, $n_c=1.505$.[8] No wavelength or temperature variations of these values have been reported so far. Two optical axes are at an angle of $\pm V$ to the c axis in the bc plane.[8] The crystal symmetry allows the natural optical activity described by the second-rank pseudotensor with only one nonzero component G_{12}.[9,10] No measurements of its value have been published.

Optical absorption of $BaMnF_4$ in the visible is dominated by Mn^{2+} $d\rightarrow d$ transitions split by the crystal field, the

first transition beginning at ~ 19000 cm^{-1}.[11] Earlier studies of linear dichroism showed a small change in slope in the temperature dependence at T_I.[5] Birefringence measurements also showed anomalous behavior of Δn_{ac} at T_I and a small shift of the transition temperature when cooling or heating the sample.[6]

At temperature near $T_I \simeq 250$ K, $BaMnF_4$ undergoes a structural phase transition. Recent theoretical analysis of different experimental data has shown that the most likely point-group symmetry of the low-temperature phase is 2 (C_2).[2,12,13] The wave vector of the order parameter of the transition was found in neutron inelastic scattering experiments[2] as $k_2 = b_2/2 + \mu b_1$ with $\mu = 0.392$; that means doubling of the unit cell along b and incommensurability along a. Vectors b_1, b_2, and b_3 are basic vectors of the reciprocal lattice.[13] Rather different data on the lattice changes at T_I were found in an x-ray study,[4] and the controversy between these two studies still is not solved; however, it appears that this is due to sample differences involving specimens grown in different laboratories.

The general analysis of the index of refraction and birefringence changes at the structural phase transition has been given in Refs. 14 and 15. In Ref. 16 it was found that the incommensurability of crystals may be a source of some new optical phenomena, e.g., the index of refraction may be wave-vector dependent, but the magnitude of these phenomena is expected to be below the sensitivity and the accuracy of our technique, and they will not be taken into account in our treatment of the data.

Since $BaMnF_4$ is improper ferroelectric and ferroelastic, we believe that the primary contributions to the index of refraction and the birefringence should be directly coupled with the order parameter and not with polarization or deformation (see below). We may evaluate these primary contributions from expressions for the interaction energy of light with $BaMnF_4$ crystals. On the basis of symmetry considerations this energy $\mathscr{E}$ may be written in a form[12]

$$8\pi \mathscr{E} = \epsilon_{ij}^0 E_i E_j + (\xi^2+\eta^2)(\rho_{aa}E_a^2 + \rho_{bb}E_b^2 + \rho_{cc}E_c^2) + (\xi^2-\eta^2)\rho_{bc}E_b E_c \ , \quad (1)$$

where $\epsilon_{ij}^0(\omega,T)$ is that part of the optical dielectric permeability which is unrelated to the two-component (ξ,η) order parameter, describing the structural phase transitions; E_i, E_j are a-, b-, and c-axis components of the electric field vector $\vec{E}$ of the light, and ρ_{ij} are phenomenological coefficients. In a more rigorous treatment the four-dimensional nature of the $BaMnF_4$ order parameter[2,13] could be displayed explicitly in Eq. (1), but those extra two dimensions introduce no qualitative effects in the energy analysis.

By differentiating Eq. (1) with respect to E_i and E_j, we obtain the principal values of the refractive index n_i and the birefringence Δn_{ij}.

$$n_i(T) = n_i^0(T) + \frac{\rho_{ii}}{2n_i^0}\langle(\xi^2+\eta^2)\rangle \ , \quad (2)$$

$$\Delta n_{ij}(T) = (n_i^0 - n_j^0) + \left[\frac{\rho_{ii}}{2n_i^0} - \frac{\rho_{jj}}{2n_j^0}\right]\langle(\xi^2+\eta^2)\rangle \ . \quad (3)$$

From these equations we see that the structural phase transition at $T_I \simeq 250$ K should change the principal values of the refractive index, n_a, n_b, and n_c, these changes being different for different principal polarizations of the light. Consequently, the same is true for the birefringence. All these changes should be proportional to the average value of the square of the order parameter, as was also proved in the general analyses.[14,15] It is important to note that due to the low symmetry of $BaMnF_4$ above T_I not only the index of refraction, but also the birefringence, which is nonmorphic,[15] will be affected by fluctuations in the order parameter, since $\rho_{ii} \neq \rho_{jj}$ and the term

$$\left[\frac{\rho_{ii}}{2n_i^0} - \frac{\rho_{jj}}{2n_j^0}\right]\langle(\xi^2+\eta^2)\rangle$$

is nonzero. That is not true for cubic materials for any direction of observation and for uniaxial crystals for light propagating along the optical axis (when for symmetry reasons $\rho_{ii} = \rho_{jj}$). In these situations only the index of refraction is affected by fluctuations above T_I (see, e.g., Ref. 17), but not the birefringence. We therefore expect in the simplest description that additional contributions to the principal values of n_i and to the birefringence Δn_{ij} should vary as the square of the space-time-averaged value of the order parameter both above and below T_I.

From Eq. (1) we see that the phase transition gives rise to a new off-diagonal component of the optical dielectric permeability

$$\epsilon_{bc} = (\xi^2-\eta^2)\rho_{bc} \ .$$

Physically that means a rotation of the optical index ellipsoid around the a axis below T_I, the angle of rotation being defined by the equation

$$\tan(2\gamma) = 2(\xi^2-\eta^2)\rho_{bc}/(\epsilon_b - \epsilon_c) \ , \quad (4)$$

where γ is the angle between old and new principal axis of the optical ellipsoid in the bc plane.

If we assume, following Refs. 12 and 13, that at the phase transition the unit cell is doubled in the bc plane, then two types of domains may be present below T_I: (1) $\xi \neq 0$, $\eta = 0$ or (2) $\xi = 0$, $\eta \neq 0$. According to Eq (2) that means that principal values of the refractive index will be modified in the same manner in both types of domains below T_I. Contrarily, the rotation of the optical ellipsoids, as follows from Eq. (4), should be in opposite directions in two types of domains.

In addition to these primary effects, which appear as a consequence of a direct coupling between the optical susceptibility and the order parameter, there must be secondary effects related to the spontaneous polarization P_i and deformation changes U_{ij} below T_I. These changes can be found from the following part φ_1 of the thermodynamic potential[12]

$$\varphi_1 = \gamma_1(\xi^2+\eta^2)P_x + (\xi^2+\eta^2)(\delta_1 U_{xx} + \delta_2 U_{yy} + \delta_3 U_{zz}) + \delta_4(\xi^2+\eta^2)U_{uz} \ . \quad (5)$$

Thus the polarization P_x will induce changes of the main values of the refractive index through linear γ_{ijk} and quadratic R_{ijkl} electro-optical effects. Other contributions to these values of the refractive index come from the photoelastic effect, which describes the changes of the refractive index under deformations. Up to now neither electro-optic nor photoelastic constants of $BaMnF_4$ have been reported, and there is no way to separate primary and secondary contributions to the refractive index from their observed values.

The distinction we make in the present paper between "primary" and "secondary" contributions to refractive index is appropriate only for $BaMnF_4$ and not for ferroelectrics or ferroelastics in general. In $BaMnF_4$, which is pyroelectric both above and below the transition temperature T_I, the change of polarization ΔP_s is extremely small, and deformation U_{ij} almost unmeasurable. But in general the change in polarization and deformation is very large at the transition temperature and the effects we call secondary may be much larger than the primary ones.

The next effect we want to discuss is the natural optical activity. As we mentioned above, in the high-temperature C_{2v}^{12} phase there is only one nonzero off-diagonal component G_{12}, which can be observed with light propagating along the optical axes.[9] Below $T_c \simeq 250$ K the lowering of the crystal symmetry that we observe in the present study gives rise to three new diagonal components of the gyration tensor, G_{11}, G_{22}, and G_{33}.[9,10] These three components could be observed as a rotation of the main axis of elliptically polarized light propagating through the crystal along the b, c, or a axis, respectively.[18,19]

III. EXPERIMENTAL

A. Interferometric technique

This technique has been described in detail in Ref. 20, and thus here we note only the most important points. The light source was a helium-neon laser operating at $\lambda = 0.6328$ μm. The apparatus permitted us to measure temperature variations of the optical path $\delta\psi = \delta\varphi\,\lambda/2\pi l$, where $\delta\varphi$ is the phase difference between the two interferometer beams and l is the crystal thickness at room temperature. This optical path variation is related to the refractive index variation δn through the equation

$$\delta n(T) = \delta\psi(T) - (n-1)\delta l(T)/l \ . \tag{6}$$

Thus lattice expansion data are needed to get $\delta n(T)$ from measured values $\delta\psi(T)$. These data have been published recently[2] for the temperature range from 4.2 to 300 K, but the accuracy of the measurements was of the order $\delta l \simeq 10^{-3}$, and no anomaly of lattice parameters was detected near the structural phase transition. The limited precision of these data is the reason that we shall analyze our original data on $\delta\psi(T)$ (see Fig. 4) and not those on $\delta n(T)$ (see Fig. 5), for which the lattice expansion data are required. We estimate the sensitivity of our technique as $\delta\psi \sim 10^{-6}$, but in prolonged measurements, owing to the slow drift of the interferometer null point, the accuracy decreased to $\delta\psi \sim 10^{-5}$.

Two different cryostats were used in the interferometric measurement. The first cryostat covered the range 20—400 K; the second cryostat covered the range 120—520 K. In both cryostats the samples were placed on an evacuated cold finger, and the sample temperature was monitored by different thermocouples with an accuracy 0.2 K. The data were registered on an XY recorder continuously as a function of temperature during slow warming or cooling of the sample. A typical curve is shown in Fig. 1.

B. Polarimetric technique

The polarimetric apparatus is schematically illustrated in Fig. 2. The optical path consists of a helium-neon laser at $\lambda = 0.6328$ μm, the polarizer, the sample, the Faraday cell modulator, the analyzer, and the photomultiplier (PM). The signal from the PM at the first harmonic of the modulator was supplied to the lock-in amplifier and was recorded as a function of temperature on the XY recorder. This installation permitted us to measure the rotation of the main axis of elliptically polarized light with a sensitivity $\delta\beta \sim 10$ sec of arc (see Fig. 3). At a crystal thickness $l \sim 1$ mm that means sensitivity $\delta\Delta n_{ij} \sim 10^{-8}$. A polarimetric technique was used for measuring the birefringence and the rotation of the main axis of elliptically polarized light (angle β) for different orientations of the polarization of incident light (angle α_0) with respect to the principal axis of the optical indicatrix. For a birefringent crystal the following relation is valid[18,19]:

$$\tan(2\beta) = \tan(2\alpha_0)\cos\Delta_{ij} \ , \tag{7}$$

where

$$\Delta_{ij} = 2\pi 1\,\Delta n_{ij}/\lambda \ .$$

IV. RESULTS AND DISCUSSIONS

A. Index of refraction and birefringence

Our results for $\delta\psi_i$ for the principal polarizations of light as a function of temperature are shown in Fig. 4. In Fig. 5 the temperature variations of the index of refraction are shown; these were derived according to Eq. (6) for the

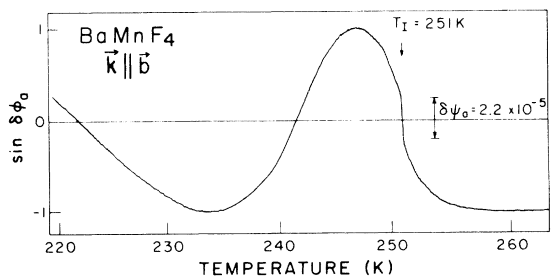

FIG. 1. Typical recording of the interferometer signal $\sin(\delta\varphi_a)$ as a function of temperature. There is a small jump of $\delta\psi_a$ at the transition point $T_I = 251$ K. The crystal thickness $t_b = 1.88$ mm; $\vec{k} \| \vec{b}$, $\vec{E} \| \vec{a}$.

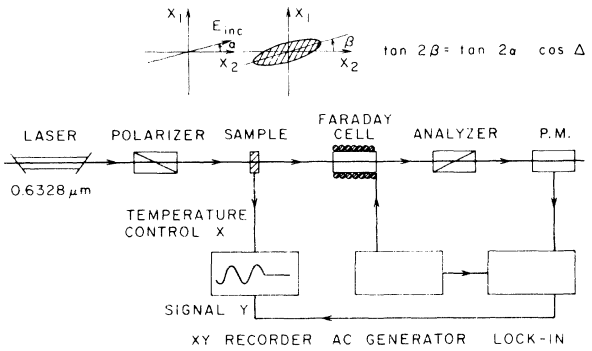

FIG. 2. Diagram of the polarimeter.

temperature range 4—300 K, where lattice expansion data are available.[2] The comparison of two sets of curves in Figs. 4 and 5 shows that the lattice expansion gives an important contribution to the variations of $\delta\psi_i$, except for $\vec{k}||\vec{a}$, since $(\delta l_a / l_a)$ shows unusually small and abnormal temperature dependence.[2] The structural phase transition manifests itself in accordance with Eq. (2) for all three curves, with different amplitudes, positive for n_a and n_b and negative for n_c. As it was shown in Ref. 15, three special linear combinations of diagonal terms of optical susceptibilities transform like the totally symmetric irreducible representation A_1 of the point group 2 (C_2). That means that observed anomalies near T_I come from the interaction with a totally symmetric amplitude mode, for example with a mode (a), whose frequency and eigenvectors are given by Eq. (12a) in Ref. 2.

For all principal polarizations of light there was a sharp change of the phase at the transition temperature. An example of the jump at T_I is shown in Fig. 1 for $\vec{E}||\vec{a}$, for other polarizations jumps were about two or three times

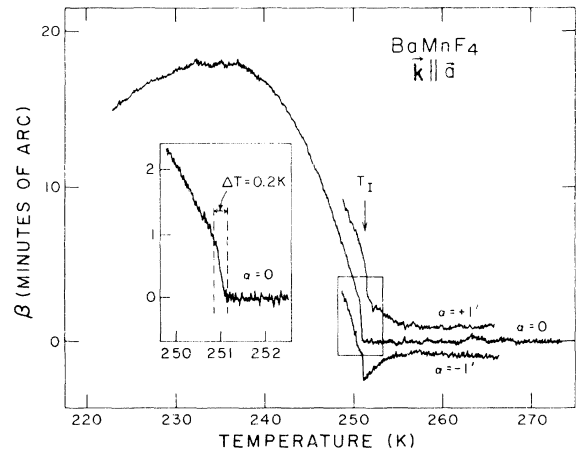

FIG. 3. Typical recording of the polarimeter signal ($\vec{k}||\vec{a}$) near T_I for different values of α_0, the angle between one of the main axes of the optical indicatrix above T_I and the direction of polarization of incident light. The sample thickness $t_a = 1.09$ mm.

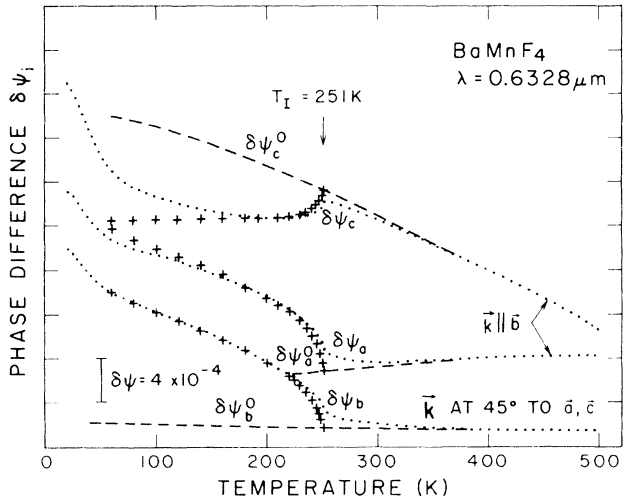

FIG. 4. Temperature variations of the phase differences $\delta\psi_i$. ●, experimental points; +, square of the order parameter from neutron data (Ref. 2).

less. These jumps prove that the phase transition at T_I has a slight first-order character. The limited precision $(\Delta T \sim 0.2$ K) of our temperature control equipment did not allow us to detect any hysteresis.

The evidence of the first-order character of the phase transition at T_I was claimed in Ref. 6, where the birefringence Δn_{ac} was studied and a kind of "jump" of Δn_{ac} in the temperature interval $\Delta T \sim 0.3$—0.4 K was seen. These data are consistent with our observation of the index of refraction jump, "diffused" over the temperature interval $T \simeq 0.2$ K. On the other hand we believe that the counterclockwise hysteresis loop for Δn_{ac} vs T (Ref. 6) may arise from temperature uncertainties, since for the first-order transition a clockwise loop is required.

The data presented in Figs. 4 and 5 clearly show large "tails" above T_I. We believe that these are due to true critical fluctuations and that their greater temperature width in comparison with the neutron scattering data[2]

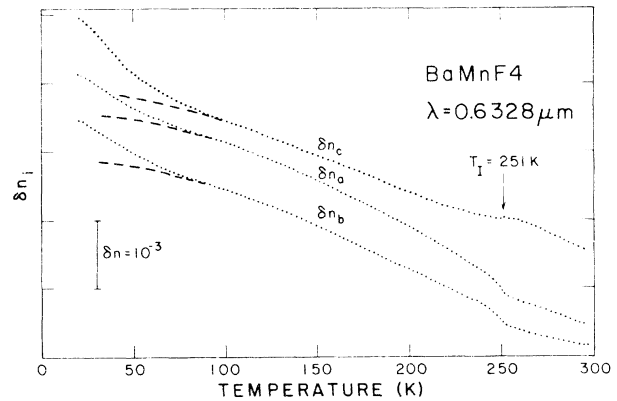

FIG. 5. Temperature dependences of the three principal values of the refractive index.

arises from the presence of all Fourier components in the measured correlation function, unlike the single wave-vector component measured[2] by inelastic neutron scattering. The quantitative analysis of the data will be given below in Sec. IV D.

The birefringence data for all three axes (Δn_{ac}, Δn_{bc}, and Δn_{ab}) are shown in Fig. 6. These data all show a sharp change in slope at T_I. The inset in this figure plots the temperature derivative $d\Delta n/dT$ and shows the discontinuity very well, but, as in the case of index refraction measurements, with an accuracy $T \simeq 0.2$ K no hysteresis effects could be noted.

B. Magnetic contribution to the index of refraction

Magnetic contribution to the index of refraction and, as a consequence, to the birefringence is now a rather well-known phenomenon. The work done in this field before 1974 was reviewed in Ref. 21 and more recently in Ref. 22. The isotropic magnetic contribution to the refraction does not depend upon the orientation of magnetization in crystals and its value is usually proportional to magnetic energy

$$\delta n^m_{\text{isotr}} \sim \langle \vec{S}_i \cdot \vec{S}_j \rangle \ . \tag{8}$$

In cubic crystals this effect can be observed only through measurements of temperature variations of the absolute index of refraction. In noncubic materials it can be seen also through measurements of birefringence. Typical values of the isotropic magnetic refraction and birefringence at low temperatures varies from $\delta n^m \sim 10^{-2}$ in oxides to $\delta n^m \sim 10^{-3}$–10^{-4} in fluorides and chlorides. The effect persists well above the magnetic transition point usually up to $T \sim (2$–$3)T_C$ (or T_N) or even higher in two-dimensional magnetics.[23,24]

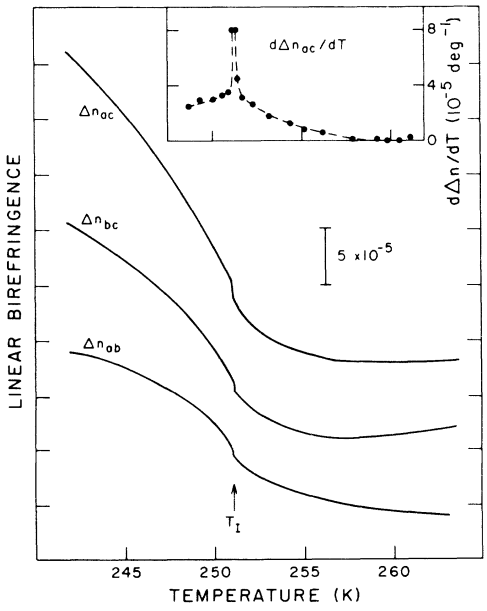

FIG. 6. Temperature variations of the birefringence near the transition temperature T_I.

The variations of the principal values of the refractive index in $BaMnF_4$ at low temperatures (see Fig. 5) clearly show the presence of the magnetic part over a wide temperature range far above the three-dimensional magnetic-ordering temperature $T_N = 26$ K. In this paper we restrict ourselves only to an approximate estimation of the magnetic contribution to the principal values of the refractive index since rather fast variations of $n_i(T)$ in the temperature range 200–100 K do not allow for a reliable extrapolation of the nonmagnetic part into the low-temperature region. These extrapolations are shown in Fig. 5 by dashed curves. From this figure we get for the isotropic magnetic contribution to the refraction at the lowest temperature 20 K: $\delta n_a^m = +4\times10^{-4}$, $\delta n_b^m = +3\times10^{-4}$, $\delta n_c^m = +10\times10^{-4}$. To our knowledge these data are the first observation of the full isotropic magnetic refraction in an optically biaxial crystal. They show that the phenomenon strongly depends upon the polarization of light. In general, such a behavior is expected for crystals of low symmetry, although no microscopic explanation has been suggested thus far.

In comparing our results with those on linear birefringence Δn_{ac} (Ref. 6) we believe that due to an inaccurate extrapolation of the lattice contribution to $\Delta n_{ac}(T)$ the magnetic contribution to the refraction in Ref. 6 was overestimated. From our results, this can be traced up to 100–120 K, but in Ref. 6 it was traced practically up to T_I. No quantitative comparison of the data is possible because in Ref. 6 they were given in arbitrary units.

Quantitative comparison of our results can be made with those for another Mn^{2+} antiferromagnet MnF_2 ($T_N = 67$ K).[20] In this uniaxial crystal

$$\delta n_a^m = \delta n_b^m = +2.7\times10^{-3} \ , \quad \delta n_c^m = +1.2\times10^{-3} \ .$$

These values are higher than those for $BaMnF_4$; that is, compatible with the higher magnetic transition temperature of MnF_2. It should be noted that in all crystals studied thus far, the magnetic contribution to the refraction was found to be positive; that is, the magnetic ordering increases the absolute values of the refractive index.

Two-dimensional magnetics show also an anomalous variation of the linear birefringence at the three-dimensional transition temperature, as was recently well established for K_2NiF_4 and other crystals.[23] This research showed that the magnitude of the sharp spike of $d(\Delta n)/dT$ at T_N is proportional to the magnetic anisotropy. In our study of the index of refraction of $BaMnF_4$ we did not find any such spike, and the explanation of its absence may be related to a small anisotropy field, since the ground state (Ref. 6) A_1 of Mn^{2+} ion is a "good" spin-only state, for which noncubic crystal field and spin-orbit splittings are usually very small.

C. Optical activity and rotation of the optical indicatrix below T_I

As we indicated in Sec. II, the change of the symmetry at T_I should be accompanied by the rotation of the optical indicatrix around the a axis; also nonzero diagonal components of optical activity pseudotensor must appear. In

order to check these predictions we made a series of experiments on the rotation $\beta(T)$ of the main axis of the elliptically polarized light as a function of temperature at different values of the angle α_0 (α_0 is the difference between the principal axis of the optical indicatrix above T_I and the polarization vector of incident light). Figure 7 shows some of the data from this study for $\vec{k}\|\vec{a}$. The temperature variation of $\beta(T)$ significantly differs for $T>T_I$ and $T<T_I$. At temperatures $T>T_I$ there was always such an angle α_0 (see curve $\alpha_0=0$ in Fig. 7) for which there was no change of the intensity of the light transmitted by the analyzer, or in other words, for which there was no rotation of the polarization of the transmitted light. Thus we can say that for $\alpha_0=0$ the polarization vector of the incident linearly polarized light is parallel to the main axis of the optical indicatrix and the position of this axis is temperature independent above T_I. Even small changes of the polarization direction of the incident beam $\Delta\alpha_0=\pm 1'$ with respect to $\alpha_0=0$ give rise to temperature variations of β, specifically at temperatures close to T_I as can be seen in Fig. 3. At larger values of $\pm\Delta\alpha_0$ the values of $\Delta\beta$ become large, $\pm\Delta\beta=\pm\Delta\alpha_0$, and the temperature variations of $\pm\Delta\beta$ are similar and satisfy the relation (7) $\beta=\alpha_0\cos\Delta$, where Δ is the phase difference.

The situation is different below $T_I=251$ K. In this case when the temperature is changed and Δ varies, the large axis of the elliptically polarized transmitted beam oscillates not around the direction 0, as it did above T_I, but around another direction 0′, which is shifted from 0 by an angle $\sim 4'$. In our opinion this is a manifestation of the rotation of optical indicatrix below T_I. At large values of $|\alpha_0|>30'$ (see curves $\alpha_0=-30'$, $\alpha_0=+30'$ in Fig. 7) the temperature variations of $\beta(T)$ are similar and are well described by Eq. (7). At small values of $\alpha_0<\pm 20'$, values of β become small, but no value of α_0 can be found at which $\beta(T)=$ const, as it was above T_I. In addition, the temperature variations of $\beta(T)$ depend on the angle α_0. In Fig. 7 one can see that the extreme values of β at large α_0 are observed at temperature T_1 (this is a point where $\Delta=0$), but at small values of α_0 these shift from T_1 to higher temperatures; and at $\alpha_0=+3.6'$, $\beta(T_1)=0$. In fact, zeros and maximum values of β are exactly reversed for $\alpha_0=3.6'$, compared with $|\alpha_0|\geq 30'$. That means that for $\alpha_0=3.6'$ at $T<T_I$, $\beta(T)\sim\sin\Delta$, as is expected for a manifestation of optical activity. Thus a complex behavior of $\beta(T)$ at small values of α_0 can be explained by a combined action of two effects: (1) by the rotation of the optical indicatrix at an angle $\sim 4'$ and (2) by natural optical activity with a nonzero component G_{33}.

For example, at $T<T_I$ and for $\alpha_0=0$, the following equation is valid for the temperature variation of $\beta(T)$:

$$\beta(T)=\gamma(T)\cos[\Delta(T)] + \{G_{33}(T)/[\tilde{n}\,\Delta n_{bc}(T)]\}\sin[\Delta(T)]\,, \tag{9}$$

where γ is the optical ellipsoid rotation angle.

Figure 8 illustrates contributions of different effects to the rotation of the large axis of the elliptically polarized light at $\alpha_0=0$ and $\alpha_0=+3.6'$. At $\alpha_0=0$ above T_I, $\beta=0$, since $\vec{E}_{inc}\|\vec{X}_2$ ($\vec{c}$) and there is no optical activity (the nonzero component G_{12} does not contribute to the rotation in this geometry). Below T_I, $\beta(T)$ depends both on the optical activity as $\sin\Delta$, and on the birefringence as $\cos\Delta$, since E_{inc} and X_2' do not coincide any more. At

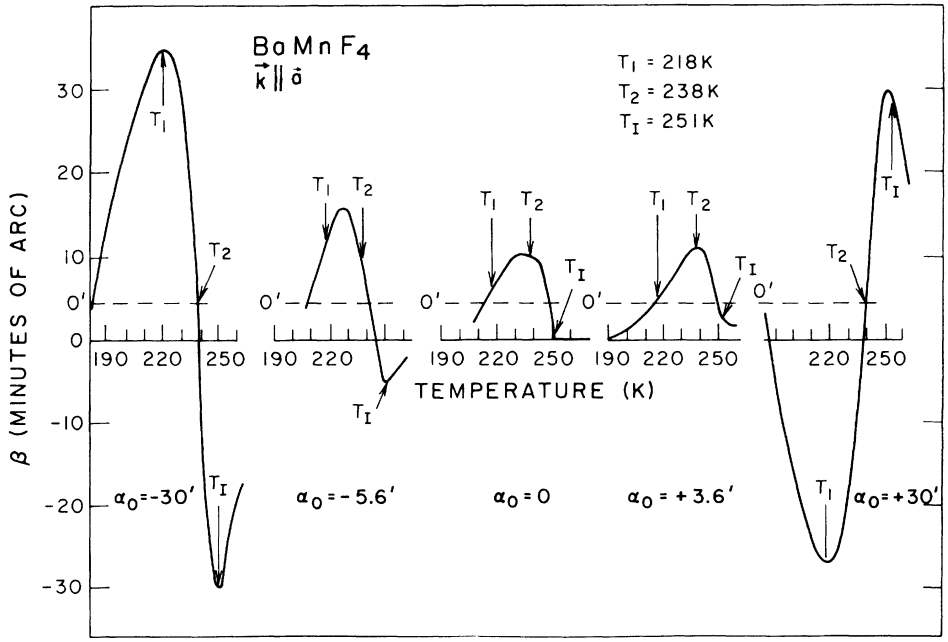

FIG. 7. Polarimetric study of $BaMnF_4$: Intensity as a function of temperature for different values of the angle of incident polarization α_0.

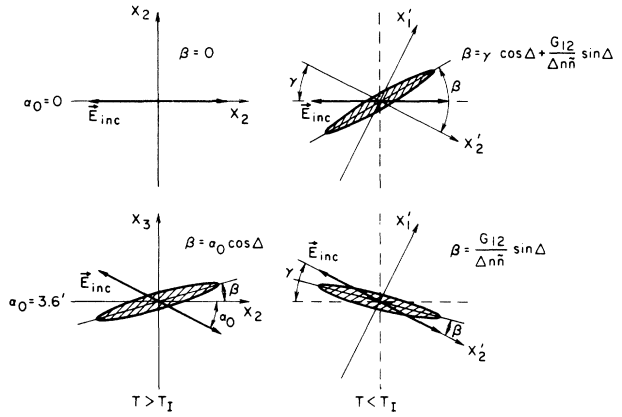

FIG. 8. Schematic explanation of different contributions to variations of intensity, shown in Fig. 7, for $\alpha_0=0$ and $\alpha_0=3.6'$. X_1, X_2 and X_1', X_2' are principal axes of optical indicatrix at $T > T_I$ and $T < T_i$, respectively. E_{inc} is the electric vector of the incident light beam. β is the angle between X_2 and the electric vector of the transmitted light beam γ is the rotation angle of the main axis of elliptically polarized light below T_I.

$\alpha_0 = +3.6'$ above T_I there is a small variation of β with temperature since E_{inc} and X_2 do not coincide. Below T_I mainly optical activity is manifested.

It should be noted that both the rotation of the optical indicatrix and the optical activity are absent above T_I and their appearance takes place exactly at T_I in the form of a very-well-pronounced small jump of $\beta(T)$. Thus no short-range-order contribution is present in these two effects, unlike the case of the refractive index and the birefringence. But since both effects are present simultaneously, we were unable to separate them in the whole temperature interval, except at fixed points $\Delta = 0, \pm\pi/2$, where $\sin\Delta = 0$ or $\cos\Delta = 0$. The separation showed us quite unexpectedly that below T_I neither γ nor G_{33} depend on temperature. Thus we see that the rotation of the optical ellipsoid does not follow Eq. (4). The experimental data suggest that above T_I, $\gamma = 0$ and $G_{33} = 0$, but at $T = T_I$ there is a jump in both these quantities to $\gamma \cong 4'$ and $G_{33} \cong 5 \times 10^{-5}$, but then below T_I they stay temperature independent, at least to $T \simeq 180$ K. In other words, they do not depend on the amplitude of the lattice distortions, as the index refraction and the birefringence do, but rather they depend on the phase mode, which in $BaMnF_4$ does not depend on temperature in the incommensurate phase below T_I.[2] More experimental and theoretical research in this field is required for quantitative understanding of observed effects.

D. Critical exponents

In this section we discuss in detail temperature variations of the refractive index around the structural phase transition temperature $T_I = 251$ K. In order to separate different contributions to the variations of $\delta\psi_i$ (see Fig. 4) we made extrapolations from the high-temperature region ~ 400–500 K, where fluctuations of the order parameter can be ignored, to the low-temperature region. In the case of $\delta\psi_a$ a simple linear extrapolation was found to be satisfactory, but for $\delta\psi_c$ the Debye function was used (shown as dashed lines in Fig. 4). The procedure of separating different contributions to the refractive index variations has been discussed earlier in Ref. 20. The difference between experimental curves and extrapolated curves is attributed to phase changes $\delta\psi_i^{\xi}$, related to the order parameter. From Fig. 4 one can see that above $T_I = 251$ K a contribution of the order parameter to $\delta\psi_i$ can be traced up to $T \simeq 350$ K for all three principal polarizations of light. A similar behavior was observed earlier for temperature variations of the refractive index[17] and photoelastic coefficients[25] in $BaTiO_3$.

Figure 9 is a plot of the relative phase lag for $\delta\psi_i^{\xi}$ versus reduced temperature above T_I. Within experimental error all three values of $\delta\psi_i$ yield (from Fig. 9) the same exponential dependence of $\frac{1}{2}$ (their mean is 0.48 ± 0.04). This value of $\frac{1}{2}$ agrees with a simple theory for δn communicated to us by A. P. Levanyuk and indicates that the qualitative features of $\delta\psi_i(T)$ mirror those of $\delta n_i(T)$, despite the difference in thermal-expansion behavior of a, b, c and axes.

In Figure 10 a comparison between optical and neutron data[2] is made for $T < T_I$, where the intensity I of the (0.39;0.5;0.5) peak was used. If there were no fluctuation effects (or defects' contributions, etc.), both neutron intensity I and phase lag $\delta\psi_i^{\xi}$ would be expected to decrease smoothly to zero at $T_I = 251$ K and remain proportional to each other. Figure 10 shows that this is true from 170 to 225 K. But above 225 K optical data depart from such a simple dependence due presumably to the integration over the wave vector in the index fluctuation term discussed earlier. At low temperatures, $T < 170$ K, no proportionality of $\delta\psi_i^{\xi}(T)$ and neutron intensity is expected, due to less reliable subtraction procedure, thermal expansion, and magnetic contributions to $\delta\psi_i(T)$.

This comparison of two sets of data, neutron and optical, clearly shows us that below T_I the anomalous part of the refractive index, which varies proportially to time-space average value $\langle\xi^2\rangle$ of the order parameter, can be decomposed into two contributions

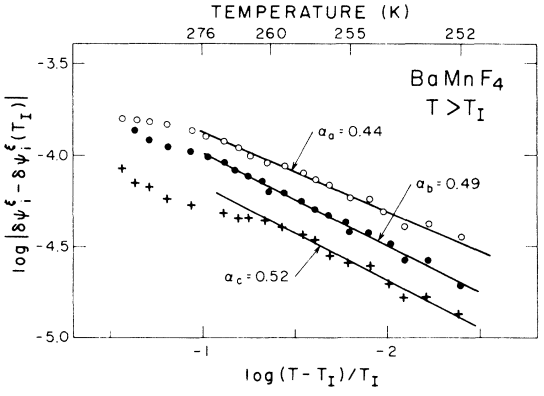

FIG. 9. Relative phase lag $\delta\psi_i^{\xi}$ vs reduced temperature above T_I.

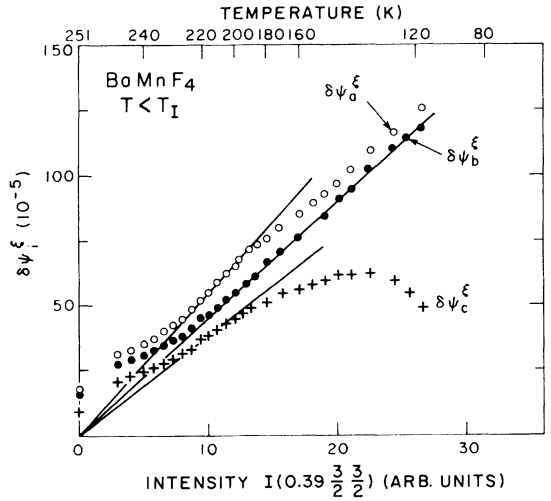

FIG. 10. Optical phase lag $\delta\psi_i^{\xi}$ vs intensity I of the (0.39;0.5;0.5) E neutron elastic peak (Ref. 2).

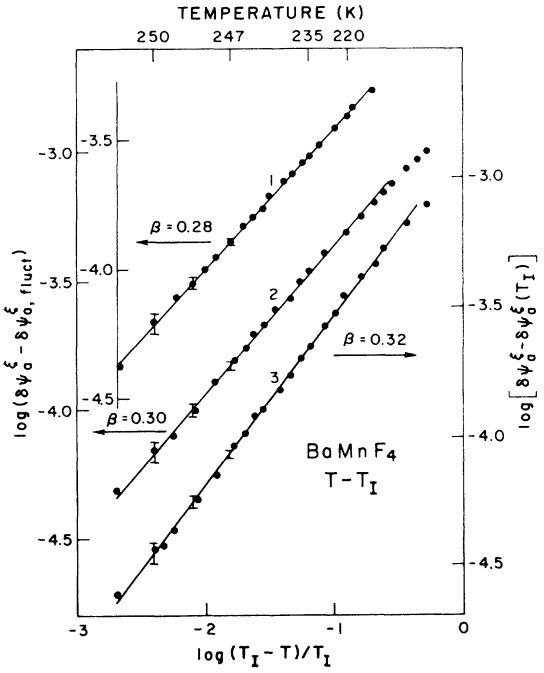

FIG. 11. Log-log plot of $\delta\psi_a^{\xi}$ obtained for different separation procedures vs reduced temperature at $T < T_I$.

$$\langle \xi^2 \rangle = \langle \xi \rangle^2 + \langle \xi^2_{\text{fluct}} \rangle \ .$$

We assumed that the fluctuation portion is exactly symmetric[26] in $T-T_I$ both above and below T_I. Then the order-parameter contribution to the phase lag may be written as

$$\delta\psi_i^{\xi}(T-\Delta T) - \delta\psi_{i,\text{fluct}}^{\xi}(T_I+\Delta T)$$

at $\Delta T \ll T_I$.

This remaining part of $\delta\psi_i$ is plotted versus reduced temperature in Fig. 11 (curve 1) for a special polarization $\vec{E}||\vec{a}$. The transition temperature $T_I=251$ K corresponds to the beginning of the "diffused" jump when approaching from the high-temperature region. This procedure gave $\beta=0.28\pm0.02$ for all three polarizations of the light. When the transition temperature was taken at the end of the diffused jump, the value of $\beta=0.30\pm0.02$ was obtained (curve 2 in Fig. 11). An even higher value of $\beta=0.32\pm0.02$ can be obtained if fluctuations of the order parameter are ignored below T_I (curve 3 in Fig. 11), as was done in Ref. 6, where the value of $\beta=0.30$ was obtained. In all three cases experimental points fall well on straight lines for the temperature interval $2.7\times10^{-3}\sim10^{-1}T_I$. We believe that the value $\beta=0.28\pm0.02$ is the most reasonable value (curve 1 in Fig. 11). The other two procedures do not take into account factors of real behavior of $\delta\psi_i$. On the other hand, it is necessary to remember that the transition at $T_I=251$ K is of a slight first order and the critical exponent β should not describe the variation of the order parameter at temperatures very close to T_I where the jump takes place ($\Delta T\sim0.2$–0.4 K).

V. SUMMARY AND CONCLUSIONS

As a result of the present study we were able to answer the questions that were put in the Introduction.

(1) The rotation of the optical index ellipsoid and the appearance of the diagonal component G_{33} of the optical activity tensor below T_I suggest that the crystal symmetry is changed at the transition from $Ama2_1$ (C_{2v}^{12}) to 2 (C_2) or even lower. Both of these effects appeared exactly at T_I in the form of a well-pronounced jump. No fluctuational contribution was seen above T_I. In contradiction with a simple theory, which predicts the rotation of the optical ellipsoid [see Eq. (4)] to be dependent on the square of the order parameter, no temperature variation of this rotation and of the G_{33} component could be seen below T_I at least to temperatures as low as ~180 K. Such a behavior resembles that of the incommensurate superlattice peak (0.39;0.5;0.5), which does not change with temperature according to neutron scattering data.[2]

(2) Measurements of different optical effects such as the two mentioned just above and also of principal indices of refraction and birefringence convinced us that the transition at T_I is slightly first order. Well-reproduced jumps have been seen in all these quantities, though no hysteresis has been observed with the accuracy $\Delta T\simeq0.2$ K.

(3) and (4) The analysis of the temperature variations of the phase lag above T_I was found to vary with a critical exponent 0.48 ± 0.04. This value gives a good fitting of experimental data for temperatures not very far away (~10–15 K) from $T_I=251$ K, though fluctuational contributions to the refractive index are distinctly seen up to 350 K. We believe that below T_I the order parameter varies with temperature with the critical exponent $\beta=0.28\pm0.02$ when the fluctuational part is accurately subtracted.

(5) We did not find any evidence of another structural

phase transition in the proximity of T_I.

Besides these results, we made estimations of the magnetic part of the refractive index at low temperatures. This contribution was found to be anisotropic, the highest value being $\delta n_c^m \simeq 1 \times 10^{-3}$, and could be traced up to ~ 120 K, e.g., to much higher temperatures than the three-dimensional magnetic-ordering temperature $T_N = 26$ K.

ACKNOWLEDGMENTS

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[26]This assumption is questionable, since fluctuations above and below T_I may differ by factors of 2 or more, but this correction to our data is not large in any case. The present procedure is obviously an improvement over fits with no subtraction, and it involves no adjustable parameters.