PHYSICAL REVIEW B VOLUME 48, NUMBER 2 1 JULY 1993-II

Optical properties and symmetry restrictions in the incommensurate phase of $[N(CH_3)_4]_2ZnCl_4$

C. L. Folcia, J. Ortega, and J. Etxebarria
Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco,
Apartado Postal 644, Bilbao, Spain

T. Breczewski
Departamento de Física Aplicada II, Facultad de Ciencias, Universidad del País Vasco,
Apartado Postal 644, Bilbao, Spain
(Received 8 February 1993)

The birefringence, optical activity, and rotation of the optical indicatrix have been measured in the normal and incommensurate phases of tetramethylammonium tetrachlorozincate $[N(CH_3)_4]_2ZnCl_4$ along the direction of the modulation wave vector. The measurements have been carried out on two different samples using a high-accuracy universal polarimeter. In contrast to previous observations a null value for the gyration in the whole incommensurate range has been found. In addition, up to the experimental error, no rotation of the indicatrix has been detected. The present work is therefore a confirmation of the view that the symmetric restrictions for tensors describing macroscopic properties of an incommensurate structure are those imposed by the point group associated to its superspace group. In this context, some remarks are made in relation to the different theoretical approaches that, contrary to this idea, permit the existence of gyration effects in centrosymmetric incommensurate systems.

I. INTRODUCTION

The existence of optical activity in materials exhibiting centrosymmetric incommensurate (INC) phases has become a controversial problem both from the theoretical and experimental points of view. In fact, in accordance with the idea that macroscopic tensors in INC structures are restricted by the point groups associated to their superspace groups, no gyration effects should occur in centrosymmetric systems. Nevertheless, since the development of the high-accuracy universal polarimeter (HAUP) by Kobayashi and Uesu,[1] gyration effects have been detected in some directions in the (centrosymmetric) INC phases of the following materials: K_2SeO_4, $(NH_4)_2BeF_4$, $[N(CH_3)_4]_2CuCl_4$, Rb_2ZnCl_4, Rb_2ZnBr_4, $[N(CH_3)_4]_2ZnCl_4$, and $(C_3H_7NH_3)_2MnCl_4$.[2–12] Moreover, rotation of the optical indicatrix, also symmetry forbidden, has been observed at the INC phases of $[N(CH_3)_4]_2CuCl_4$,[2] $MnBaF_4$,[13] and $(CH_3)_3NCH_2COO\cdot CaCl_2\cdot 2H_2O$ (BCCD).[14] Consequently, in order to explain these results, different theoretical treatments, principally based on the spatial dependence of the gyration and dielectric tensors in INC structures, have been proposed in the literature.[8,10,15,16]

Contrary to the results referred to above, further measurements performed by means of the HAUP technique on Rb_2ZnBr_4 and $[N(CH_3)_4]_2CuCl_4$ have shown the absence of optical activity at the INC phase of these compounds[17] in agreement with conventional symmetry requirements. In view of this situation, a definite understanding of the general behavior of gyration effects in INC systems is urgently needed. This requires not only a systematic investigation on different materials, but also an adequate clarification of the measurement procedure with the HAUP technique in order to remove possible contradictions. In this paper we report on a detailed study of optical activity and rotation of the optical indicatrix in the INC phase of $[N(CH_3)_4]_2ZnCl_4$ along the direction of the modulation wave vector. The measurements have been performed at the normal and INC phases of this material using a HAUP system built up in our laboratory.

$[N(CH_3)_4]_2ZnCl_4$ belongs to the A_2BX_4 family and shows near room temperature a sequence of INC and ferroelectric phases characterized by a structural modulation of wave vector $\mathbf{q}=\delta\mathbf{c}^*$. The ferroelectric phase is due to the lock in of the INC modulation wave vector at the commensurate value $\mathbf{q}=\frac{2}{5}\mathbf{c}^*$. This phase has space group $Pc2_1n$ with spontaneous polarization along the $\mathbf{b}$ direction.[18] This sequence is limited between two commensurate phases with space groups $Pcmn$ and $P112_1/n$ for the high- and low-temperature limits respectively.[18] The normal-INC and INC-ferroelectric transitions take place at about 24 and 7 °C, respectively.

On the other hand, $[N(CH_3)_4]_2ZnCl_4$ is the INC material that most extensively has been studied with the HAUP technique. Up to four different values of the gyration coefficient G_{13} with different temperature behaviors have been reported in the literature.[2,5,9,11] The behavior of G_{33} in the INC phase of $[N(CH_3)_4]_2ZnCl_4$ was measured by Dijkstra[10] and also by Dijkstra, Kremers, and Meekes.[11] These results show a clearly variable value for G_{33} not only in the INC, but also in the high-temperature normal phase. This anomalous behavior in the normal phase is understood by the authors to reflect precursive effects above the normal-INC transition temperature. These effects are interpreted as a consequence of fluctuations of the soft mode whose insta-

0163-1829/93/48(2)/695(6)/$06.00

bility defines the structural distortion which determines the INC phase.

In contrast to the above results, we have found a zero value for G_{33} in the whole temperature range under study. Furthermore, no rotation of the optical indicatrix could be detected. It is not straightforward to justify the reason of such serious discrepancies. A possible explanation could be given if we take into account that the case of $[N(CH_3)_4]_2ZnCl_4$ is rather complicated to deal with experimentally. This is because the birefringence of this material passes through zero at the middle of the INC phase. As follows from the HAUP theory, a small birefringence can introduce the appearance of important spurious contributions in the final results that are especially difficult to remove. This point will be further discussed in a later section.

This paper is organized as follows. In the next section we briefly describe the experimental setup and measuring method. The data processing and analysis of the raw measurements is explained in Sec. III, where the final results for birefringence, optical activity, and indicatrix rotation are also presented. Finally, in Sec. IV, our results are compared with previous studies and recent theoretical approaches allowing for nonzero gyration effects in centrosymmetric INC phases are briefly reviewed and discussed.

II. EXPERIMENTAL SETUP

Single crystals of $[N(CH_3)_4]_2ZnCl_4$ were grown from an aqueous solution at 42 °C using a dynamic method.[19] Large colorless crystals exhibiting clear natural faces were obtained. Platelike-shaped specimens were cut in the directions of the (001) plane, i.e., with the main faces perpendicular to the (pseudohexagonal) c axis. The surfaces were polished to optical quality using diamond paste with a grain size of 1 μm.

The HAUP device utilized in the present study has been described in detail elsewhere.[17] Briefly, the light generated by a 10-mW He-Ne laser ($\lambda = 633$ nm) passes through a polarizer, the sample suitably oriented, and an analyzer. The light is circularly polarized before entering the polarizer, and the transmitted intensity is detected by a photomultiplier. The polarizers are Glan-Thompson prisms mounted on rotating stages driven by continuous high-resolution motors. An encoder motor controller guarantees a reproducibility of the angular positions within $\pm 8.1 \times 10^{-6}$ rad for each motor movement. The temperature of the sample was controlled by means of a N_2 open-flow cryogenic system (Cryostream, Oxford Cryosystem),[20] allowing for a temperature stability of about 0.1 K. It is worth mentioning that this temperature controller is specifically designed for x-ray-diffraction measurements, where samples are much smaller than the crystals utilized in the present work. Nevertheless, it is well known that no optical components can be placed between the sample and the polarizers when using the HAUP technique, and therefore a conventional cryostat cannot be employed. In fact, as has been previously shown,[17] even the small residual-strain birefringence of the cryostat windows can produce systematic errors which make the final results completely unreliable.

The measurement process was as follows. For each temperature a global linear least-squares fit of the transmitted intensity detected by the photomultiplier as a function of θ, the angle between the polarizer and the sample fast axis, and Υ, the relative polarizer-analyzer angle, was performed following the procedure described in Refs. 21 and 22. These angles were varied in such a way that the resulting (θ, Υ) region was centered at the minimum of the transmitted intensity.[17,22] This procedure allows for the determination of the following quantities:[5]

$$\theta_0 = -\tfrac{1}{2}(p+q)\cot(\Delta/2) - (1/2)\delta\Upsilon + \theta \ , \quad (1)$$

$$A = 4\sin^2(\Delta/2) \ , \quad (2)$$

$$B = -(2k-\gamma)\sin\Delta + 2\delta\Upsilon\cos^2(\Delta/2) \ , \quad (3)$$

$$C = B/\sin\Delta = -(2k-\gamma) + \delta\Upsilon\cot(\Delta/2) \ ; \quad (4)$$

where Δ and k are defined as

$$\Delta = (2\pi/\lambda)\Delta n\, d \quad (5)$$

and

$$k = (G/2\bar{n})\Delta n \ . \quad (6)$$

Here Δ is the phase difference between the fast and slow components of light propagating through the sample. G, Δn, and $\bar{n}$ [$=1.527$ (Ref. 11)] are the optical activity, birefringence, and mean refractive index of the sample, respectively, d the sample thickness, and λ the light wavelength in vacuum. p and q stand for the parasitic ellipticities of the polarizer and analyzer, $\gamma = p - q$, and $\delta\Upsilon$ is a kind of "effective" deviation angle from the crossed polarizers position, which arises principally as a result of mechanical drifts of the motor drivers or sample roughness.[21,22] θ_0 is the polarizer position corresponding to minimum light intensity between crossed polarizers (referred to an arbitrary origin) and θ represents the rotation of the indicatrix (except for a constant).

In order to detect any possible sample or thermal history dependence of the results, two different crystals of $[N(CH_3)_4]_2ZnCl_4$, referred to as samples 1 and 2, were employed in the present study. Crystals thicknesses were 1.466±0.001 and 1.432±0.001 mm for samples 1 and 2, respectively, and their areas were about 30 mm^2 in both cases. The thermal history of the samples was the following. Sample 1 was cooled down into the ferroelectric phase, and measurements were performed on heating starting at 9 °C in the INC phase. Sample 2 was heated up to 35 °C, and the measurements were made on cooling from 34 °C in the high-temperature normal phase. In both cases the temperature was varied step by step at intervals of 1 and 2 °C in the INC and normal phases, respectively. The time required at a given temperature to scan the desired set of (θ, Υ) values was about 45 min.

III. EXPERIMENTAL RESULTS

The birefringence Δn, along the (001) direction, was derived from (2) and (5) together with an independent measurement of the absolute optical retardation and the sign of $d\Delta/dT$ at room temperature using a Berek compensator. Δn values are represented in Fig. 1 for heating (sample 1) and cooling (sample 2) runs. The results are in good agreement with those previously reported.[11] The slight difference between both curves observed in the figure can be attributed to experimental conditions, such as temperature gradients, position of the laser spot in the sample, or different size and shape of the crystals, which become important in an open-flow temperature controller system. It can be pointed out here that, contrary to other quantities such as the dielectric susceptibility, global thermal hysteresis in the INC phase is not expected to be significant for birefringence measurements. In fact, Δn depends on the modulus of the order parameter, whose evolution with temperature is practically not affected by metastable states or defects responsible for hysteresis phenomena.[23] Finally, two important points must be commented on: First, the normal-INC phase transition temperature T_c can be clearly detected, Δn remaining almost constant in the normal phase. Second, Δn goes through zero at a given temperature T_Δ in the INC phase. As will appear below, these two aspects become relevant in order to derive and interpret optical activity and indicatrix rotation results from the collected data. For instance, the presence of the error $\delta\Upsilon$ is responsible for a divergence of C just at T_Δ as a result of the $\cot(\Delta/2)$ in expression (4).

Optical activity is calculated from expressions (4) and (6) once the errors $\delta\Upsilon$ and γ are obtained. The method normally employed in order to determine these parameters in systems such as $[N(CH_3)_4]_2ZnCl_4$, where the phase under study is limited by another one which lacks of optical activity ($k=0$), is to perform a linear fit of C vs $\cot(\Delta/2)$ in this normal phase.[5] Moreover, it should be pointed out that, because of symmetry requirements, optical activity for $[N(CH_3)_4]_2ZnCl_4$ along the (001) direction should be zero not only at the normal, but also at the low-temperature ferroelectric phase. Nevertheless, the described method was found to be nonapplicable here since Δn and consequently Δ are almost constant at the normal phase (see Fig. 1). Therefore the small Δ-varying range prevents us from obtaining a reliable C vs $\cot(\Delta/2)$ straight line in this temperature region. On the other hand, the Δ range could not be enlarged by considering the ferroelectric phase since the existence of ferroelectric domains greatly complicates the application of the HAUP measurement method in that region.

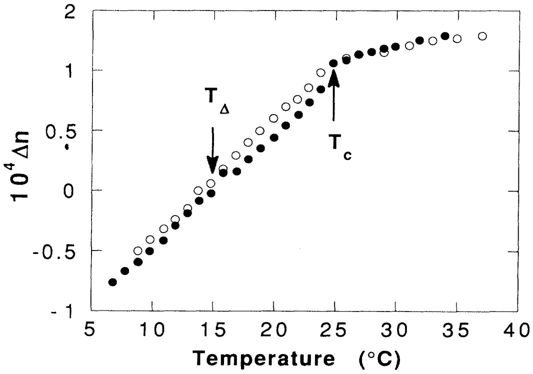

FIG. 1. Birefringence Δn vs temperature of $[N(CH_3)_4]_2ZnCl_4$ along (001). Open circles correspond to the data obtained on heating for sample 1, whereas solid circles represent the results on cooling for sample 2. The arrows indicate the temperatures corresponding to the normal-INC transition (T_c) and $\Delta n=0$ (T_Δ).

The existence of a $\Delta=0$ temperature in $[N(CH_3)_4]_2ZnCl_4$ allows, however, for a direct determination of $\delta\Upsilon$ from expression (3). Thus $\delta\Upsilon$ in both measurements was obtained directly from the value of B in (3) at T_Δ, i.e., $\delta\Upsilon=B/2$. Using this procedure, $\delta\Upsilon$ values resulted in being $(3\pm1)\times10^{-4}$ and $(3\pm5)\times10^{-5}$ for samples 1 and 2, respectively. In order to evaluate γ for sample 1, we multiplied expression (4) by Δ, considering the normal phase ($k=0$), and performed a fit of $(C-\delta\Upsilon\cot(\Delta/2))\Delta$ $(=\gamma\Delta)$ vs Δ to a straight line passing through the origin. The parameter γ for sample 1 was determined to be $\gamma=(3.4\pm0.3)\times10^{-3}$. On the other hand, it was not possible to determine γ for sample 2 by considering expression (4) at the normal phase exclusively, such as in sample 1, because the points were much too scattered. Nevertheless, it resulted that the set of data corresponding to the INC phase could be well fitted to a linear Δ-dependent function if the whole temperature range was considered. According to expression (4), this implies a constant value for k at the INC phase. Furthermore, taking into account that the normal-INC phase transition is continuous, it is expected that k cannot change steeply at T_c and, therefore, the proportionality between $(C-\delta\Upsilon\cot(\Delta/2))$ and Δ in the INC range suggests a small k value in this temperature region. By using this procedure, the parasitic contribution γ for sample 2 was found to be $\gamma=(1.50\pm0.06)\times10^{-3}$. In order to confirm qualitatively the k size estimated from the data of sample 2, we plotted $-(2k-\gamma)\Delta$ vs Δ with the results of sample 1. It was found that the complete set of points corresponding to the normal as well as INC phases could be reasonably fitted by the same linear Δ-dependent function at both phases. Accordingly, k results in being small and nearly constant at the INC phase also in this case.

The optical activity for both samples is represented in Fig. 2. Error bars were calculated by means of usual error propagation techniques starting from the standard deviations obtained at the fitting procedure for parameters A, B, and C. It can be noted that error bars show a divergence just at T_Δ. This is consistent with a divergence of C at that temperature and is due to the fact that the indetermination of the extinction directions increases considerably as Δn goes to zero. As can be seen, clearly different curves are obtained for samples 1 and 2, although error bars overlap for temperatures higher than 12 °C. At lower temperatures, however, the optical activity for sample 1 decreases down to its minimum value $G=-2.5\times10^{-7}$, while the result corresponding to sample 2 indicates a slight tendency to positive values. If only curve 1 were considered, it could be concluded that optical activity is present in the INC phase of

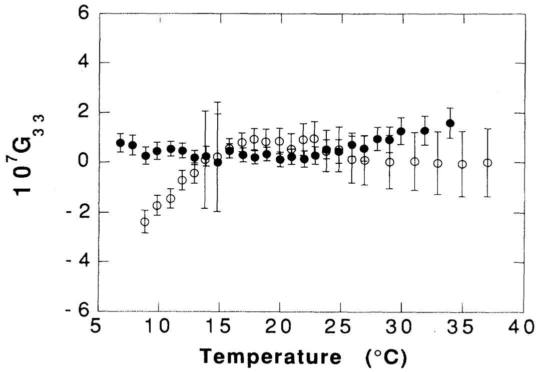

FIG. 2. Optical activity vs temperature of $[N(CH_3)_4]_2ZnCl_4$ along (001). Open circles correspond to the data obtained on heating for sample 1, whereas solid circles represent the results on cooling for sample 2.

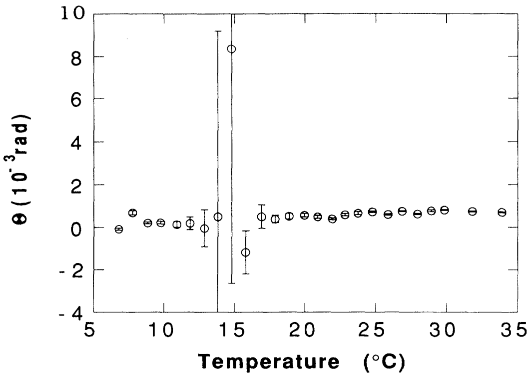

FIG. 3. Optical indicatrix rotation θ vs temperature of $[N(CH_3)_4]_2ZnCl_4$ along (001). The value of θ at 34 °C has been arbitrarily set to zero. The singularity of θ at 15 °C is due to the passage of Δ through zero at this temperature.

$[N(CH_3)_4]_2ZnCl_4$ and that its modulus decreases significantly on heating from the ferroelectric phase. Nevertheless, taking into account the second curve, it seems more realistic to conclude that the observed effects result from external causes other than the intrinsic behavior of the material. In fact, an order of magnitude of 10^{-7} for the optical activity means a maximum rotatory power value of about 0.05 °/mm, which could be explained in terms of external factors such as stress, temperature gradients, etc. A plausible interpretation to the gradual variation observed in curve 1 could also be given if the fact that the crystal was heated from the ferroelectric phase is taken into account. The apparent existence of optical activity in the INC phase of $[N(CH_3)_4]_2ZnCl_4$ could be a consequence of the coexistence of ferroelectric and INC phases in a considerable temperature range[24] as well as of the presence of domain walls in the ferroelectric regions, which are expected to result in parasitic contributions distributing the different measured optical parameters.[22] In accordance with this hypothesis, it is close to the ferroelectric phase (where symmetry requires $G_{33}=0$) that the apparent optical activity for sample 1 presents its maximum value (in modulus) within the INC phase. On further heating, since the presence of domain walls and phase coexistence regions are expected to be greatly reduced, the observed G value reduces gradually (see Fig. 2).

On the other hand, an apparent increase of optical activity for sample 2 in the normal high-temperature phase, resembling the precursive effects previously mentioned,[11] can be also observed in Fig. 2. Nevertheless, since this effect appears to be clearly sample dependent and taking into account the error bars, it can be concluded that the non-null values of G in the normal phase of sample 2 are just a consequence of the particular calculation process rather than a real effect. Therefore the conclusion is the same with both samples: There is no measurable optical activity at the INC phase of $[N(CH_3)_4]_2ZnCl_4$ along the (001) direction.

Finally, the rotation of the indicatrix, θ, was calculated from expression (1). In principle, the parasite $(p+q)/2$ can be obtained from a linear fit of θ_0 vs $\cot(\Delta/2)$ in the high-temperature normal phase, where θ is expected to remain constant with temperature. Nevertheless, in our case it was not possible to perform this fit considering only the normal phase since, as was pointed out above, Δ is practically constant in the normal phase so that the scattering of the experimental points did not allow for a reasonable fit. Nevertheless, it also appeared here that θ_0 vs $\cot(\Delta/2)$ could be linearly fitted if the whole temperature range was considered. This result implies that θ presents in the INC phase the same constant behavior as in the normal one. The indicatrix rotation for sample 2 is represented in Fig. 3 (the results corresponding to sample 1 are not included in the figure because no definite conclusion could be drawn because of the experimental noise). Error bars were calculated by standard error propagation techniques. Consequently, with the above result, a constant behavior for θ is observed in the whole temperature range of the measurement, corresponding therefore to a null rotation of the indicatrix. Scattering of points close to T_Δ, as well as a divergence of the error bars for these points, are only a consequence of the divergence of the term $\frac{1}{2}(p+q)\cot(\Delta/2)$ in the expression for θ_0.

IV. DISCUSSION

As has been mentioned in the Introduction, the first measurements of the optical activity in $[N(CH_3)_4]_2ZnCl_4$ along the (001) direction were reported by Dijkstra.[10] However, these results showed a divergence of G at the $\Delta=0$ temperature as a clear consequence of the existence of the parameter $\delta\Upsilon$, which was not taken into account in the calculations.[15] Further measurements performed on this material by Dijkstra, Kremers, and Meekes,[11] where the influence of $\delta\Upsilon$ was properly considered present a similar qualitative behavior to the data appearing in Fig. 2 for sample 1, although our G values are smaller roughly by a factor of 2. Regarding the shape of the curves, the most important difference between both sets of data is the behavior of G at the normal phase. While we have essentially $G=0$, these authors found a nonzero optical activity, whose absolute value increases linearly with temperature. This is interpreted as a consequence of the already mentioned precursive effects. Curiously, a similar trend occurs with the points of our sample 2 at this temperature region, although, again, our G values are smaller and have just the opposite sign. We consider, however, that precursive effects cannot be responsible for such a behavior since they are due to the fluctuations of the mode that softens at the normal-INC phase transition and, consequently, should be important only near the transition point. From our point of view, given the size of the error bars and the temperature dependence displayed by samples 1 and 2, the only reachable conclusion is that the optical activity is null both in the normal and INC phases.

This absence of optical activity would be in accordance with the idea that gyration tensors in INC materials are symmetry restricted in a conventional manner, i.e, by the point group associated with their superspace group. In particular, if the INC crystal is centrosymmetric, the optical activity should be zero. Along this line, it is interesting to comment on some recent theoretical models[8,10,15,16] which permit the appearance of gyration effects in INC structures with inversion symmetry. Here we will briefly review and discuss such theories.

One of these models, proposed by Kobayashi,[16] predicts the existence of optical activity in INC structures by claiming the presence of helicoidal atomic arrangements in the crystal due to the inhomogeneity of the order parameter which describes the normal-INC phase transition. However, we consider that this argument is not justified at all. The order parameter is an element of an abstract space whose unique condition is to reflect the symmetry of a low-temperature phase respect to a prototype phase. In the case of INC structures, the order parameter is typically two dimensional and its phase varies linearly along the crystal in the direction of the modulation wave vector. In a hypothetical three-dimensional space x,y,z, where x and y refer to the two components of the order parameter and z is oriented along the crystal **c** direction, it is clear that the tip of the order parameter vector would describe a helix. Nevertheless, this is only an *ad hoc* geometrical construction in order to force a helix and it has nothing to do with the fact that the atoms of the structure are actually ordered in a helicoidal fashion. On the other hand, it is obvious that once the existence of a real helicoidal arrangement is assumed, the appearance of optical activity becomes an elementary matter (see, e.g., Ref. 25).

An alternative theoretical treatment to the one proposed by Kobayashi has been developed by investigators at the Nijmegen University.[8,10,15] The starting point of their approach is the spatial inhomogeneity of the dielectric tensor.[8,15] The selection rules imposed by the INC superspace group are applied to the long-wavelength Fourier components of this tensor. Furthermore, the existence of one distinguishable so called mesoscopic coherence length l_0 ($l_0 \sim 1-100$ nm) in the INC structure[15] is assumed, and the complete set of Fourier wave vectors whose wavelength is close to l_0 is considered. By averaging the contributions of this set of Fourier wave vectors, an expression is obtained for a modulated dielectric tensor with wavelength l_0. Furthermore, it can be demonstrated that whenever a sample is assumed to contain a particular number of such wavelengths, constant across its entire surface, the dielectric tensor inhomogeneity can eventually produce an apparent gyration effect, even if the actual gyrotropic tensor is not taken into account.[10,15] Nevertheless, two important objections can be made to this approach.

(a) The reciprocal vectors (h,k,l,m) corresponding to the most significative of the considered Fourier wave vectors have high values of the m indices (for example, $m=5$ for $[N(CH_3)_4]_2ZnCl_4$). Therefore it is not clear to what extent the contribution of these Fourier components to any gyration effect could be relevant. Although it is not the case for $[N(CH_3)_4]_2ZnCl_4$, optical activity in other centrosymmetric INC materials has claimed to be as high as that of α-quartz (see, e.g., Refs. 6–8).

(b) The assumption that the coherence length l_0 fits into the crystal thickness, in such a way that the number of these coherence lengths remains constant across the entire sample surface, does not seem to be justified in a real crystal. Instead of that and taking into account the small l_0 value, it appears more realistic to assume that the number of these coherence lengths depends strongly on the point of the sample surface. In this situation and even within the framework of this theory, it is obvious to conclude that the measured optical activity must cancel out to zero in any practical situation.

In summary, the measurements presented in this paper indicate that there is neither measurable optical activity nor indicatrix rotation in the whole range of the INC phase of $[N(CH_3)_4]_2ZnCl_4$ along the (001) direction. Some previous studies carried out on Rb_2ZnBr_4 and $[N(CH_3)_4]_2CuCl_4$ with the HAUP technique also indicate the absence of optical activity in the centrosymmetric INC phase of these materials.[17] These results are supported by some theoretical works which, in contrast to the above models, show that a microscopic theory of light propagation in INC structures cannot explain nonzero values for the optical activity in centrosymmetric phases.[26] Likewise, it has been explicitly shown that the indicatrix rotation, although locally existing in INC materials, is averaged out to zero if the structure is orthorhombic.[27] These conclusions are also in agreement with conventional symmetry requirements as far as the fact that the symmetry group describing any macroscopic property must include the point group associated with the space or superspace group of the structure.[28] The present work is therefore a confirmation of the view that the symmetry restrictions for tensors describing macroscopic properties are similar both for commensurate and INC materials.

ACKNOWLEDGMENTS

One of us (J.O.) thanks the Basque Government for financial support. This work is supported by the Basque Government (Project No. 063.310-0962-C02-02/91).

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