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1995 J. Phys.: Condens. Matter 7 421

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## Optical activity in the incommensurate and ferroelectric phases of $\text{Rb}_2\text{ZnCl}_4$

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Received 1 July 1994, in final form 11 October 1994

**Abstract.** The birefringence and optical activity of  $\text{Rb}_2\text{ZnCl}_4$  have been measured in the normal, incommensurate and ferroelectric phases. The measurements have been carried out using a high-accuracy universal polarimeter (HAUP). In contrast to previous observations, an essentially null  $g_{13}$  gyration coefficient (setting  $Pcmn$ ) has been obtained in the incommensurate phase ( $g_{13} < 5 \times 10^{-6}$ ), and no measurable change has been detected on entering the ferroelectric phase. Optical parameters, estimated in this phase using a classical point dipole–dipole polarizability theory, are consistent with the observed behaviour. In addition, a reprocessing of the previously reported measurements also shows that, within the experimental error, the resulting optical activity value is in agreement with ours. The conclusions deduced from the present study, together with from some recently published results on gyration effects in centrosymmetric incommensurate phases, support the view that optical activity, like any other macroscopic property, is symmetry restricted by the point group associated with the structure. Possible release from this rule when considering point defects in real incommensurate structures is also discussed.

### 1. Introduction

In recent years the optical properties of incommensurate (INC) materials have been investigated extensively [1]. In particular, much attention has been devoted to the study of the anisotropy of the optical susceptibilities (especially birefringence and optical activity), since this provides helpful information about structural changes in these materials. Among the phenomena related to the optical anisotropy, the existence of optical activity (OA) in centrosymmetric INC phases has become one of the most controversial and challenging problems from both the theoretical and experimental points of view (see [2]–[4] and references therein). On one hand, some theoretical approaches allowing for the existence of OA in these materials have appeared in the literature [5–8] in spite of the fact that conventional symmetry restrictions forbid any gyration effect [9, 10]. On the other hand, the measurement of OA in INC structures is rather complicated even with the high-accuracy universal polarimeter (HAUP) method [11, 12], because the gyration coefficients are typically 1000 times smaller than the birefringence.

In fact, in all INC materials studied so far by more than one investigation group, the data reported by the different authors disagree with each other. For example, according to [13] and [14] no measurable OA appears in the INC phase of  $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$  along the direction of the modulation wave vector. Nevertheless, in other works clear gyration has been observed in this direction [7, 15] and a somewhat smaller effect appears in the measurements

reported in [16] and [17]. The case of  $\text{Rb}_2\text{ZnBr}_4$  is also interesting. Measurements of all the gyration components  $g_{ij}$  revealed null values for all except  $g_{13}$  (setting  $Pcmn$ ) [18]. Furthermore, it must be stressed that the size reported for this coefficient (see also [5]) implies an OA in the INC centrosymmetric phase of the same order of magnitude as that of  $\alpha$ -quartz. This greatly contrasts with further studies carried out by us, in which no gyrotropy could be detected in the INC phase of this material [4].

In view of this situation, it is evident that more experimental data are necessary to elucidate the general behaviour of the optical activity in INC structures. Moreover, it is our view that an adequate clarification of the measurement procedure with the HAUP method is still required in order to remove contradictions.

III	192 K	II	302 K	I
<b>Ferroelectric</b>		<b>Incommensurate</b>		<b>Normal</b>
$\mathbf{q} = \mathbf{c}^*/3$		$\mathbf{q} = \delta \mathbf{c}^*$		$\mathbf{q} = 0$
$Pc2_1n$		$Pcmn(00\delta)(ss-1)$		$Pcmn$

Figure 1. The phase sequence, transition temperatures, and symmetry groups of  $\text{Rb}_2\text{ZnCl}_4$  in the relevant temperature range.

In this paper we present a detailed study of the birefringence and gyration in the INC phase of  $\text{Rb}_2\text{ZnCl}_4$ . This material presents the phase sequence shown in figure 1. In the INC (II) phase the modulation wavevector is directed along the  $c$  axis,  $\mathbf{q} = \delta \mathbf{c}^*$  [19]. The ferroelectric (III) phase is due to the lock-in of the INC modulation at the commensurate value  $\delta = \frac{1}{3}$ . The spontaneous polarization takes place along the  $b$  axis.

The investigation of  $\text{Rb}_2\text{ZnCl}_4$  is interesting for several reasons. First, it is one of the most prominent examples of the  $A_2BX_4$  family and, consequently, has attracted most of the studies of the various physical properties in INC crystals. Secondly, the OA was studied previously by Kobayashi and co-workers [20], and, according to this work,  $g_{13}$  is non-zero throughout all the INC range, having an order of magnitude similar to that reported for the isomorphous compound  $\text{Rb}_2\text{ZnBr}_4$  [18]. However, the temperature dependence of  $g_{13}$  reported in these works is completely different for the two compounds, which seems somewhat strange. Finally, given the similarity between  $\text{Rb}_2\text{ZnCl}_4$  and  $\text{Rb}_2\text{ZnBr}_4$ , the presence of gyrotropy in  $\text{Rb}_2\text{ZnCl}_4$  appears to be inconsistent with our null result found for  $\text{Rb}_2\text{ZnBr}_4$  [4].

This paper is organized in the following way. In section 2 the experimental method and measuring process are briefly described. The analysis of the experimental data together with the results for the birefringence and OA are presented in section 3. A theoretical estimate of the refractive indices and OA in the ferroelectric phase, based on the available structural information, is presented in section 4. The results are discussed in section 5, including an exhaustive comparison with the measurements of the previous study referred to above. Finally, we draw our conclusions in section 6.

## 2. Experimental details

Single crystals of  $\text{Rb}_2\text{ZnCl}_4$  were grown at 315 K from an aqueous solution using a dynamic

method [21]. Large crystals with well developed natural faces and of good optical quality were obtained. The sample was a plane parallel plate, with dimensions  $2 \times 2 \times 0.402 \text{ mm}^3$ , whose surfaces were polished with diamond paste with a grain size of  $1 \mu\text{m}$ .

According to the group at Waseda University [2–6],  $g_{13}$  is the only non-zero gyration coefficient in the INC phase. These authors have found this to be a general rule for all  $A_2BX_4$  compounds showing the sequence  $Pcmn-Pcmn(0, 0, \delta)(s, s, -1)-Pc2_1n$ . In this situation, the maximum value of the OA is attained for a direction that makes an angle  $\theta = 45^\circ$  with respect to the  $a$  axis, since the OA is given by  $G = g_{13} \sin 2\theta$ . Therefore, in principle, the best direction for measuring the OA is that corresponding to  $\theta = 45^\circ$ . However, this direction is rather close to the optic axis at room temperature, and, therefore, problems could arise when using the HAUP technique in a broad temperature range. In order to avoid these difficulties, the normal to the plate was lying on the  $a$ - $c$  plane in our sample and made an angle of  $\theta = 30^\circ$  with respect to the  $a$  axis. On the other hand, along this direction,  $\sin 2\theta$  is not far from unity (0.867) so the OA of the crystal is only a small percentage lower than the maximum attainable value.

The OA in the INC phase is thus given by

$$G = \sin 60^\circ g_{13}. \quad (1)$$

The HAUP device has been described in detail elsewhere [4, 13]. A 10 mW He-Ne laser of wavelength 632.8 nm was used as a light source. The temperature of the sample was controlled by means of an  $N_2$  openflow cryogenic system (Cryostream, Oxford Cryosystems) [22], which permits a temperature stability of 0.1 K. The system of data collection and analysis is also explained in [4]. For each temperature, the quantities

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

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

were determined from the global linear least-squares fit of all the raw data following the procedure described in [23]. In (2) and (3)  $\Delta$  is the optical retardation and  $\gamma = p - q$ , where  $p$  and  $q$  are the parasitic ellipticities of the polarizer and analyser.  $\delta Y$  is an 'effective' deviation angle from the crossed polarizers position, which presumably arises as a result of small inaccuracies in the micropositioning system of the polarizers or surface roughness of the sample [23, 24]. The birefringence  $\Delta n$  and OA are obtained using the equations

$$\Delta = (2\pi/\lambda)\Delta nd \quad k = G/2\bar{n}\Delta n \quad (4)$$

where  $d$  is the sample thickness,  $\bar{n}$  the mean refractive index and  $\lambda$  the light wavelength in vacuum.

The measurements were performed on cooling from 335 K down to 125 K in steps of 2 K. The time required at a given temperature to scan the desired set of  $11 \times 11$  polarizer positions varied between 35 and 45 min.

### 3. Experimental results

The birefringence  $\Delta n$  versus temperature is shown in figure 2. These values were obtained from (2) and (4) together with a measurement at room temperature of the absolute optical retardation and the sign of its derivative with temperature. The results are consistent with

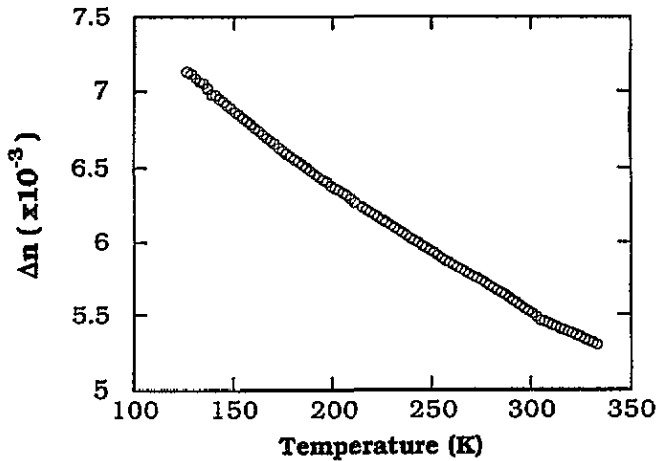


Figure 2. The temperature dependence of the birefringence  $\Delta n$  of  $\text{Rb}_2\text{ZnCl}_4$  measured along a direction perpendicular to the  $b$  axis, and making an angle of  $30^\circ$  with respect to the  $a$  axis.

those previously reported [25,26]. A linear variation of  $\Delta n$  with temperature is observed within the normal, INC and ferroelectric phases. The normal-INC phase transition is clearly detected.  $\Delta n$  showing different slopes in the two phases. However, no anomalies in the behaviour of  $\Delta n$  can be appreciated in the INC-ferroelectric phase transition. This behaviour is also in accordance with [26], where only very small jumps of  $\Delta n$  ( $\sim 10^{-6}$ ) were observed.

The OA was calculated from expression (3) once the errors  $\delta Y$  and  $\gamma$  were removed. The method normally employed in order to determine these parameters is to perform a linear fit of the values  $B/\sin \Delta$  versus  $\cot(\Delta/2)$  in the normal phase. In this phase the OA must be zero by symmetry requirements and  $\delta Y$  and  $\gamma$  are directly obtained from the slope and intercept of the straight line [12]. In our case, however, the change of  $\Delta$  in the normal phase is small and therefore this procedure is inaccurate. Nevertheless  $\delta Y$  can be obtained by a different process. The open circles in figure 3 show  $B$  versus  $\Delta$  (3). The  $\delta Y$  value is extracted from  $B$  at  $\Delta = 8\pi$  since at this temperature  $B = 2\delta Y$ . An analogous method was employed in a quite similar situation [13]. Using this procedure,  $\delta Y$  turned out to be  $(1.3 \pm 0.1) \times 10^{-3}$ . It is interesting to check the consistency of the values of  $B$  measured. As indicated in (3)  $B$  must be zero at the points  $\Delta = 7\pi$  and  $\Delta = 9\pi$  since  $\cos^2(\Delta/2) = \sin \Delta = 0$ . As can be seen in figure 3 this is fulfilled by our data rather well.

The solid circles in figure 3 show the quantity  $2\delta Y \cos^2(\Delta/2)$ . Clearly the two curves depicted in this figure are similar in the whole range. This coincidence means that the value of  $B$  is almost exclusively due to the contribution of  $\delta Y$ , which is in agreement with the fact that the  $B$  curve presents a maximum at  $\Delta = 8\pi$ .

Figure 4 shows  $B$  (open circles) and  $B - 2\delta Y \cos^2(\Delta/2)$  (solid circles) versus temperature. The second curve, which is equal to  $-(2k - \gamma) \sin \Delta$ , is below  $5 \times 10^{-4}$  and presents a noisy appearance in the whole range of temperature. Taking into account the scattering of points and the uniform behaviour of the curve, even in the normal phase, in which  $k = 0$ , it is not possible to consider  $2k$  different from zero in the whole temperature range under study. A very smooth undulation is, however, appreciable, which can be explained in terms of a small contribution from  $\gamma$ . In any case,  $2k$  is expected to be smaller than  $5 \times 10^{-4}$  for both the INC and lock-in phases. Using (1) and (4), a value of  $g_{13} < 5 \times 10^{-6}$  is obtained in the INC range. Although the symmetry permits a non-zero

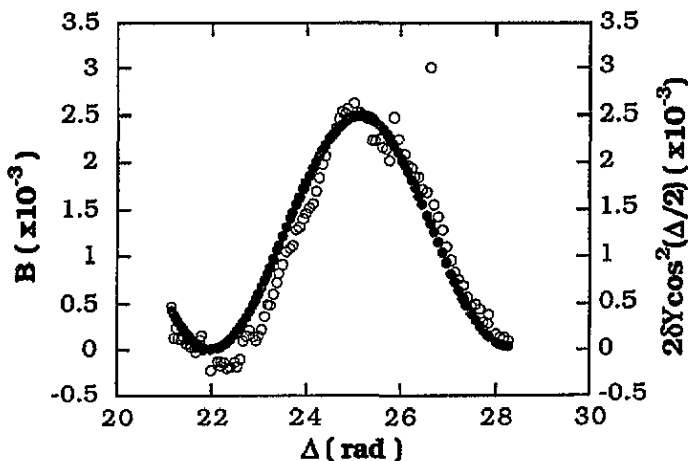


Figure 3.  $B$  (open circles) and  $2\delta Y \cos^2(\Delta/2)$  (solid circles) as functions of  $\Delta$ ,  $\delta Y$  was calculated from the  $B$  value at  $\Delta = 8\pi$ .

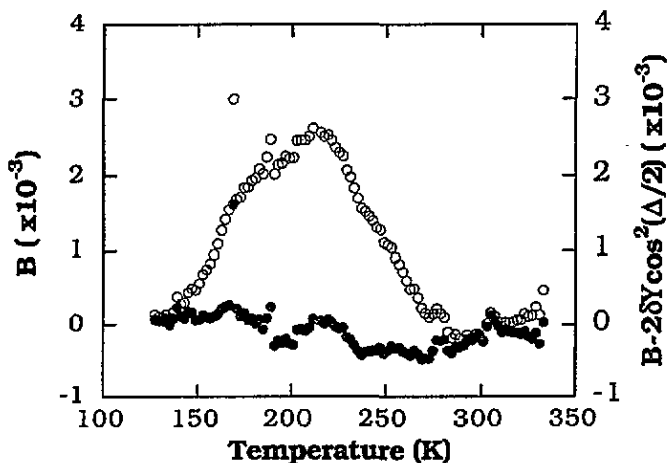


Figure 4. The temperature dependence of  $B$  (open circles) and  $B - 2\delta Y \cos^2(\Delta/2)$  (solid circles).  $\delta Y$  was calculated to be  $(1.3 \pm 0.1) \times 10^{-3}$ .

$g_{13}$  value in the ferroelectric phase, the same upper bound can be given for this coefficient in this phase.

#### 4. Optical activity calculations in the ferroelectric phase

From the results of the preceding section we deduce that  $Rb_2ZnCl_4$  shows a null value for the OA in the three phases under study. In the normal and INC phases, this is in agreement with classical symmetry requirements. It could be argued, however, that the present results are not sufficiently accurate to determine a non-null measurable value for the OA in the ferroelectric phase, where conventional symmetry conditions permit the existence of a non-zero  $g_{13}$  coefficient. Moreover, no different behaviour for the OA could be detected in the

ferroelectric and INC phases and, therefore, the conclusion about the null gyration in the INC phase would not be fully justified.

In order to investigate this point more thoroughly, we made a theoretical estimate of the magnitude of this coefficient by using the available theories that allow for calculating the optical properties (refractive indices and OA) in commensurate crystals [27]. The calculations were carried out utilizing a computer program (OPTACT) based on a classical point dipole-dipole polarizability theory, which gives rather good results when working with inorganic compounds [27–30]. The program computes the gyration tensor and refractive indices using as input data the light wavelength and the atomic coordinates and polarizabilities. The usual way of working with OPTACT is to adjust the polarizabilities by trial and error until good agreement is obtained with the experimental optical parameters.

Since the atomic polarizabilities in the ferroelectric phase are unknown, we estimated their values assuming that they are equal to those in the normal phase. The latter were calculated with OPTACT by using the experimental data for the OA ( $g_{ij} = 0$ ) and refractive indices ( $n_a = 1.560$ ,  $n_b = 1.564$ ,  $n_c = 1.574$  for a wavelength  $\lambda = 633$  nm at 310 K, which were measured with an Abbe refractometer). Taking the structural data for the normal phase given in [31], the resulting polarizabilities were  $\alpha(\text{Rb}) = 1.733 \text{ \AA}^3$ ,  $\alpha(\text{Zn}) = 0.265 \text{ \AA}^3$  and  $\alpha(\text{Cl}) = 3.195 \text{ \AA}^3$ . Now, making use of these values and taking the atomic coordinates of the ferroelectric phase at 100 K [31], the following optical parameters were finally obtained:  $n_a = 1.576$ ,  $n_b = 1.578$ ,  $n_c = 1.597$  and  $g_{13} = 4.3 \times 10^{-7}$ .

As can be seen, the order of magnitude of the birefringence is in accordance with the observed values ( $10^{-2}$ – $10^{-3}$  [26]). Also, it can be checked that the general trend of the temperature dependence of the birefringence along the three principal directions agrees reasonably well with the experimental data [26]. On the other hand, and more interestingly, the small size for the gyration coefficient is remarkable. The  $2k$  value deduced from the  $g_{13}$  coefficient is  $2k = 3 \times 10^{-5}$  for our measuring direction. Although, given the approximations we have made, a certain inaccuracy for  $2k$  can be expected, it is clear that the obtained order of magnitude is correct and reliable. Since this small magnitude for  $2k$  is not experimentally accessible with the present accuracy of the HAUP technique, it is not surprising we have not been able to detect any OA change between the normal, INC and ferroelectric phases. Therefore, we conclude that, up to the experimental capability of the existing HAUP polarimeters, there is no measurable OA in either phase of  $\text{Rb}_2\text{ZnCl}_4$ .

## 5. Discussion

The (essentially) zero OA value obtained in this work for  $\text{Rb}_2\text{ZnCl}_4$  strongly disagrees with that previously reported for this material by Kobayashi and co-workers [20], who determined for a [101] sample  $2k$  values reaching  $2 \times 10^{-3}$  in the INC phase and  $-3.5 \times 10^{-3}$  in the ferroelectric phase. As has been shown above, this last  $2k$  value is also in disagreement with our theoretical calculations. In view of such an important discrepancy, it seems of interest to analyse these results thoroughly. Since the initial  $\Delta$  and  $B$  points, from which the OA is deduced, are available in that work we have considered it appropriate to reprocess those data here in order to compare the results and look for the possible sources of the discrepancy.

Figures 5 and 6 represent respectively the results for  $\Delta$  and  $B$  obtained by Kobayashi *et al* for a [101] 0.243 mm thick plate of  $\text{Rb}_2\text{ZnCl}_4$  (figure 2(a) and (b) in [20]). Only the points corresponding to the same temperature in both original figures have been reproduced

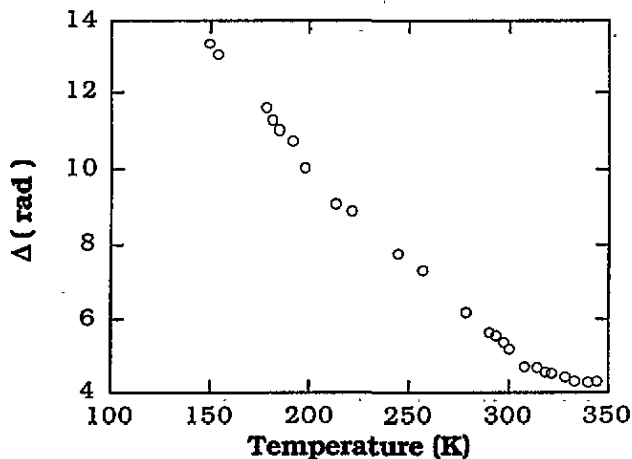


Figure 5. The temperature dependence of  $\Delta$  for a [101] 0.243 mm thick plate of  $Rb_2ZnCl_4$  according to [20].

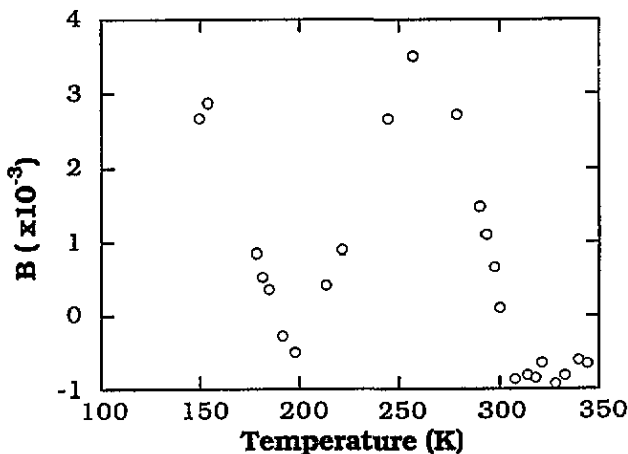


Figure 6. The temperature dependence of  $B$  for a [101] 0.243 mm thick plate of  $Rb_2ZnCl_4$  according to [20].

in figures 5 and 6. Although many points had to be discarded, the number of data depicted in figures 5 and 6 is large enough to represent well the trend of the original curves.

Starting from figures 5 and 6,  $B$  against  $\Delta$  is represented in figure 7 (solid points). The general behaviour of  $B$  in figure 7 is similar to that observed in figure 3 of [20]. Nevertheless, two important differences surprisingly arise. The points corresponding to the normal phase ( $\Delta < 5$  in figure 7) are much more compressed than in figure 3 of [20], as a consequence of the small variation of  $\Delta$  in this phase (see figure 5). In addition, the second maximum in figure 7 is somewhat higher than in the original work.

The method employed by Kobayashi *et al* in order to calculate the parasitic errors  $\delta Y$  and  $\gamma$  was to perform a linear fit of  $B/\sin \Delta$  against  $\cot(\Delta/2)$  in the normal phase (figure 4 in [20]). Nevertheless, when this procedure was carried out with the data represented in



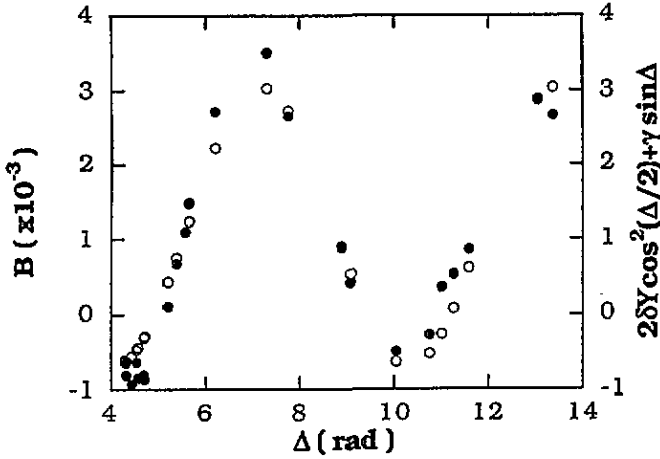


Figure 7.  $B$  as a function of  $\Delta$  obtained from the data depicted in figures 5 and 6 (solid circles) and the parasitic contribution to  $B$ ,  $2\delta Y \cos^2(\Delta/2) + \gamma \sin \Delta$  (open circles).  $\delta Y$  and  $\gamma$  were calculated to be  $1.18 \times 10^{-3}$  and  $1.46 \times 10^{-3}$  respectively.

figure 7, we found that the small  $\Delta$  range in the normal phase prevented us from obtaining a reliable  $B/\sin \Delta$  against  $\cot(\Delta/2)$  straight line in this temperature region, similarly to what happened with our measurements. This result contrasts strongly with the behaviour represented in figure 4 of [20], where the points are clearly aligned. Alternatively,  $B/\sin \Delta$  against  $\cot(\Delta/2)$  is represented in figure 8 for the whole temperature range under study. The open circles, which appear compressed in figure 8, are those corresponding to the normal phase. It is obvious that no conclusion concerning  $\delta Y$  and  $\gamma$  can be obtained by considering only the set of open circles. Nevertheless, as can be seen, the set of data in figure 8 can be fitted well to a linear function if the whole temperature range is considered. According to expression (3), this implies a constant value for  $k$  in the INC and ferroelectric phases. Furthermore, taking into account that the normal-INC phase transition is continuous, it is expected that  $k$  cannot change steeply at the normal-INC phase transition and, therefore, the linear behaviour observed in figure 8 suggests a small  $k$  value in the INC and ferroelectric phases. From the linear fit of the points represented in figure 8  $\delta Y$  and  $\gamma$  were determined to be  $\delta Y = 1.18 \times 10^{-3}$  and  $\gamma = 1.46 \times 10^{-3}$ . This  $\delta Y$  value is in good agreement with that obtained by Kobayashi *et al* ( $\delta Y = 1.2 \times 10^{-3}$ ) although  $\gamma$  is different ( $\gamma = -2.0 \times 10^{-3}$ ).

Open circles in figure 7 represent the parasitic contribution to  $B$ , that is,  $2\delta Y \cos^2(\Delta/2) + \gamma \sin \Delta$ . The small difference between this curve and  $B$  (solid circles) clearly indicates that, in accordance with figure 8, the resulting  $B$  can be almost exclusively attributed to the parasitic errors  $\delta Y$  and  $\gamma$  and, therefore,  $k$  turns out to be practically negligible. The  $2k$  value obtained from the difference between the two curves in figure 7 is represented in figure 9. It is evident that, considering the scattering of the resulting values, no conclusion can be drawn about a non-null value for  $k$  in the whole temperature range. Figure 9 must be compared with figure 5 of [20], where the result for  $2k$  obtained by Kobayashi *et al* is depicted. It can be observed that besides the scattering of the data represented in figure 9, the resulting  $2k$  values obtained by Kobayashi *et al* are about five times larger.

The origin of the discrepancy in the results of  $2k$ , calculated from the same set of experimental data, is not obvious at all. In spite of the differences in the data processing

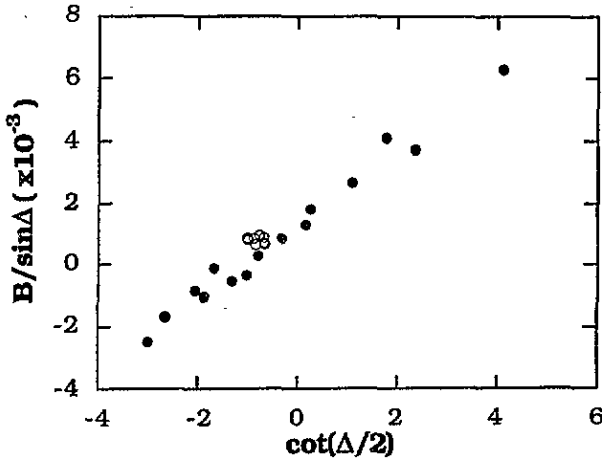


Figure 8.  $B/\sin \Delta$  against  $\cot(\Delta/2)$  obtained from the data depicted in figures 5 and 6. Open circles correspond to the normal phase. Solid circles correspond to the INC and ferroelectric phases.

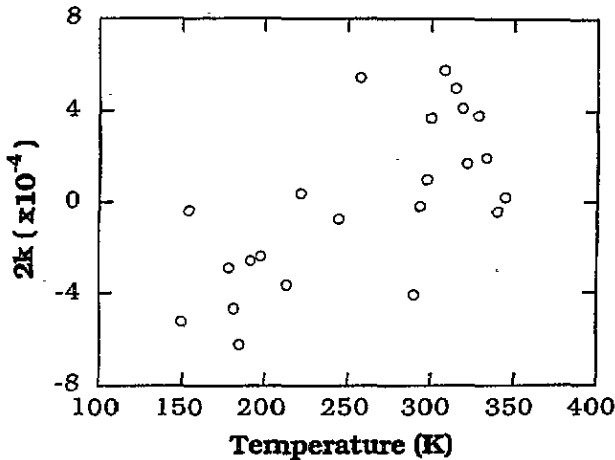


Figure 9. The temperature dependence of  $2k$  obtained from the difference between the curves represented in figure 7 (see also [20]).

indicated above, the only remarkable disagreement between the parasites calculated here and those reported by Kobayashi *et al* is the value obtained for  $\gamma$ , which turned out to be different in absolute value and sign. Nevertheless, this parameter only plays the role of an additive constant and, therefore, it does not affect the temperature dependence of  $2k$ , which, however, does critically depend on  $\delta Y$ . Consequently, it seems that an error, impossible to establish with the available information took place during the data manipulation in [20].

The conclusions deduced from the present study for  $Rb_2ZnCl_4$ , as well as other experimental results concerning OA in centrosymmetric INC phases [4, 13], clearly reinforce the classical view that the symmetry restrictions for OA are given by the point group of the structure. On the other hand, taking into account the discrepancies pointed out here, we

consider it essential to perform an exhaustive and detailed revision of the methodology and criteria employed in the HAUP technique. This point is crucial since, as is well known, small errors in the removal of parasitic contributions and data processing can eventually result in completely different conclusions.

In this respect, it is also interesting to point out that although several theoretical approaches have appeared in the literature [5–8] permitting the existence of gyration in centrosymmetric INC systems, it is questionable whether they can explain any observable effect in practice. We have discussed these theories in previous works [4, 13] and will not repeat our criticisms here.

Recently, however, it has been argued that local spatial distortions of the modulation due to point defects may give rise to OA (and indicatrix rotation) in structures where these properties are forbidden by symmetry [32]. In fact, the optical properties of  $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$  have been shown to be somewhat sensitive to defect concentration [17]. Likewise, some predictions of the theory, such as the appearance of anomalies in the OA at points where  $\Delta = 2\pi m$  with an integer  $m$ , have been observed in multidomain ferroelectric phases [33, 34]. In fact, within the framework of this model, an INC centrosymmetric structure is approximated by a succession of enantiomorphous domains, in which the long-range order is broken by point defects. Nevertheless, while the approach seems reasonable to describe multidomain phases, it is not straightforward to suppose that it is also valid for INC phases, especially in the sinusoidal regime. On the other hand, the divergences at  $\Delta = 2\pi m$  can also have an experimental origin rather than being produced by intrinsic properties of the sample. In fact, it is at these points where the optical equipment imperfections produce the largest systematic errors, whose  $\Delta$  dependence is completely similar to that predicted by the theory. In this context, it is our experience that the  $\delta Y$  error can change its value by about  $10^{-3}$  between successive phases with different domain structures [35]. This can be explained in terms of the domain wall contribution to the  $\delta Y$  value [24]. In any case, the model predicts very small OA in INC materials with an inversion centre. Numerical estimates yield  $2k$  values of the order of  $10^{-5}$  and  $10^{-4}$  for  $\text{Rb}_2\text{ZnBr}_4$  and  $\text{Rb}_2\text{ZnCl}_4$  respectively [32], which are outside or at the limit of the capability of the present experiments. Probably, this theory could account for the OA detected in other materials, such as  $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$  along the [101] direction ( $G \sim 10^{-7}$ ) [14], although other alternative explanations can also be suggested to justify such a small effect [13]. In no case, however, can the model explain a non-zero  $g_{33}$  value in this material as reported in [15]–[17], since, although each domain is acentric, it lacks OA along [001].

## 6. Concluding remarks

The measurements presented in this paper indicate the absence of any measurable OA ( $g_{13}$ ) in the whole range of the INC phase of  $\text{Rb}_2\text{ZnCl}_4$ . A conservative upper bound for the  $g_{13}$  value could be  $5 \times 10^{-6}$ . In the ferroelectric phase, the same upper limit can be given. On the other hand, a theoretical estimate for the OA in the ferroelectric phase indicates that the  $2k$  value is smaller than the accuracy that can be presently achieved with a HAUP polarimeter. The apparent discrepancies with previous measurements [20] have been exhaustively analysed. A re-examination of these data has led us to conclude that, within the experimental error, they are in agreement with our measurements. These results together with previous studies carried out in  $\text{Rb}_2\text{ZnBr}_4$ ,  $[\text{N}(\text{CH}_3)_4]\text{CuCl}_4$  and  $[\text{N}(\text{CH}_3)_4]\text{ZnCl}_4$  [4, 13] support the view that the symmetry restrictions for tensors describing macroscopic properties are similar both for commensurate and INC materials. Possible release from this rule when considering

defects in the actual structures [17, 32] has also been discussed. Although in this respect the problem seems to be still open, it is concluded that the modulation distortions can only bring about very small effects, which should be unobservable in most cases.

## Acknowledgments

We acknowledge J M Pérez-Mato for his critical reading of the manuscript. One of us (JO) thanks the Basque Government for financial support. This work is supported by the Comisión Interministerial de Ciencia y Tecnología (CICYT) of Spain (project No PB91-0554).

## References

- [1] Cummins H Z 1990 *Phys. Rep.* **185** 211
- [2] Kobayashi J 1991 *Phase Transitions* **36** 95
- [3] Dijkstra E 1991 *PhD Thesis* Nijmegen University
- [4] Ortega J, Etxebarria J, Zubillaga J, Brezewski T and Tello M J 1992 *Phys. Rev. B* **45** 5155
- [5] Meekes H and Janner A 1988 *Phys. Rev. B* **38** 8075
- [6] Kobayashi J 1990 *Phys. Rev. B* **42** 8332
- [7] Dijkstra E 1991 *J. Phys.: Condens. Matter* **3** 141
- [8] Dijkstra E, Janner A and Meekes H 1992 *J. Phys.: Condens. Matter* **4** 693
- [9] Pérez-Mato J M, Madariaga G and Tello M J 1984 *Phys. Rev. B* **30** 1534
- [10] Pick R M 1990 *Geometry and Thermodynamics: Common Problems in Quasi-Crystals, Liquid Crystals and Incommensurate Systems* ed J C Toledano (New York: Plenum) p 439
- [11] Kobayashi J and Uesu Y 1983 *J. Appl. Crystallogr.* **16** 204
- [12] Kobayashi J, Kumoni H and Saito K 1986 *J. Appl. Crystallogr.* **19** 377
- [13] Folcia C L, Ortega J, Etxebarria J and Brezewski T 1993 *Phys. Rev. B* **48** 695
- [14] Saito K, Takahashi N, Kamiya I and Kobayashi J 1993 *Phys. Rev. B* **48** 10038
- [15] Dijkstra E, Kremers M and Meekes H 1992 *J. Phys.: Condens. Matter* **4** 715
- [16] Kushnir O S, Shopa Y I and Vlokh O G 1993 *Europhys. Lett.* **22** 389
- [17] Kushnir O S, Shopa Y I, Vlokh O G, Polovinko I I and Sveleva S A 1993 *J. Phys.: Condens. Matter* **5** 4759
- [18] Kobayashi J, Saito K, Takahashi N and Kamiya I 1994 *Phys. Rev. B* **49** 6539
- [19] Gesi K and Iizumi M 1979 *J. Phys. Soc. Japan Lett.* **46** 697
- [20] Kobayashi J, Saito K, Fukase H and Matsuda K 1988 *Phase Transitions* **12** 225
- [21] Laudise R A 1970 *The Growth of Single Crystals* (Englewood Cliffs, NJ: Prentice-Hall)
- [22] Cosier J and Glazer A M 1986 *J. Appl. Crystallogr.* **19** 105
- [23] Moxon J R L and Renshaw A R 1990 *J. Phys.: Condens. Matter* **2** 6807
- [24] Moxon J R L 1990 *PhD Thesis* Oxford University
- [25] Günter P, Sanctuary R and Rohner F 1982 *Phys. Status Solidi* **a** **70** 583
- [26] Kroupa J and Fousek J 1985 *Japan. J. Appl. Phys.* **24** 787
- [27] Devarajan V and Glazer A M 1986 *Acta Crystallogr. A* **42** 560
- [28] Stadnicka K, Glazer A M and Koralewski M 1987 *Acta Crystallogr. B* **43** 319
- [29] Stadnicka K, Glazer A M, Koralewski M and Waklyn B M 1990 *J. Phys.: Condens. Matter* **2** 4795
- [30] Stadnicka K, Madej A, Tebbut I J and Glazer A M 1992 *Acta Crystallogr. B* **48** 16
- [31] Hedoux A, Grebille D, Jaud J and Godefroy G 1989 *Acta Crystallogr. B* **45** 370
- [32] Kushnir O S and Vlokh O G 1993 *J. Phys.: Condens. Matter* **5** 7017
- [33] Vlokh O G, Kushnir O S and Shopa Y I 1992 *Ferroelectrics* **16** 97
- [34] Kushnir O S, Shopa Y I and Vlokh O G 1993 *Ferroelectrics* **143** 187
- [35] Etxebarria J 1992 unpublished