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Influence of incommensurate modulation on the optical properties of the solid solution $((CH_3)_4N)_2ZnCl_{2.8}Br_{1.2}$

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This paper reports on measurements with a high-accuracy universal polarimeter of the birefringence, optical activity, and indicatrix rotation in incommensurately modulated $((CH_3)_4N)_2ZnCl_{2.8}Br_{1.2}$ crystals. It is shown that in this solid solution the inversion symmetry is broken already in the paraelastic phase, due to the inhomogeneous distribution of Cl and Br over the zinc-halide tetrahedra. This, however, allows one to study the influence of the incommensurate modulation on a nonzero optical activity. This influence is clearly shown for a sample in which, moreover, the modulation wave vector is believed to lock at several commensurate values. [S0163-1829(96)03129-3]

I. INTRODUCTION

Crystals of the solid solution $((CH_3)_4N)_2ZnCl_{4-x}Br_x$, $0<x<4$, can be considered to be members of the family of A_2BX_4-type crystals that have a β-K_2SO_4 structure at high temperatures. In the neighborhood of room temperature a phase transition occurs to an incommensurately modulated structure with modulation wave vector $\vec{q}=\gamma\vec{c}^*$, for the crystals with $x<3$.[1] It is important to realize that a description in terms of the β-K_2SO_4 structure[2] neglects the difference between Cl and Br. Each zinc-halide tetrahedron in the crystal can only contain an integral number n of bromine atoms. For a general value of x there is, therefore, a distribution of these tetrahedra $ZnCl_{4-n}Br_n$ with different values n, such that the average value of n is equal to x. The corresponding relative concentrations ρ_n were determined from Raman scattering experiments by van Loosdrecht and Janner.[3] Thus, if one takes the difference between Cl and Br into account, all lattice translational symmetry and point group symmetry are generally lost already in the high-temperature phase. Although this has only subtle effects on x-ray diffraction experiments,[2] we show in this paper that it has definite consequences for the optical properties of these crystals.

Our interest in A_2BX_4-type crystals with an average β-K_2SO_4 structure lies in the occurrence of an incommensurately modulated phase. In a broader context it is our aim to investigate the influence of an (incommensurate) modulation on the physical properties of such crystals. It is not possible to use a normal space group description for the incommensurate phase, because the presence of the modulation breaks the lattice translational symmetry. Such a symmetry can, however, be recovered if the crystal is embedded in a so-called superspace which has a dimension larger than 3. The symmetry of the structure can accordingly be described by means of a superspace group.[4–7] Many members of the A_2BX_4 family, considered here, have superspace group symmetry $Pcmn(00\gamma)(1s\bar{1})$. The point group of the structure that is obtained by averaging the effect of the modulation in the incommensurate phase is mmm. The average structure is, therefore, orthorhombic and centrosymmetric. If one is able to detect optical properties that are symmetry forbidden by the point group mmm, a clear influence of the incommensurate modulation has been found. We have recently investigated the optical properties of $((CH_3)_4N)_2ZnCl_4$ (Ref. 8) and $((CH_3)_4N)_2CuCl_4$ crystals.[9] This was done with a high-accuracy universal polarimeter (HAUP) that is very well suited for this purpose.[9–12] In the case of $((CH_3)_4N)_2CuCl_4$ a rotation of the optical indicatrix was detected in the incommensurate phase, which contradicts an orthorhombic symmetry. In addition, (small) optical activity was found which contradicts the presence of an inversion center.[13] For the case of $((CH_3)_4N)_2ZnCl_4$, however, no macroscopic symmetry breaking with respect to the average structure could be detected.

In this paper we report on similar HAUP measurements on $((CH_3)_4N)_2ZnCl_{2.8}Br_{1.2}$ crystals. These have been performed for the following reasons. As explained above, one can expect that in this solid solution deviations can occur from the macroscopic point group symmetry mmm of the average structure. The crystal can, therefore, show nonzero optical activity and indicatrix rotation even in the high-temperature phase. Instead of searching for a deviation from zero in the incommensurate phase as has been done for $((CH_3)_4N)_2ZnCl_4$, it is, therefore, possible to study the deviation from a nonzero behavior in the case of $((CH_3)_4N)_2ZnCl_{2.8}Br_{1.2}$. Though there is still disagreement on the presence of optical activity in in the incommensurate phase of $((CH_3)_4N)_2ZnCl_4$,[8] the results presented in this paper for $((CH_3)_4N)_2ZnCl_{2.8}Br_{1.2}$ show, undoubtedly, that optical activity can be affected by the modulation. Moreover, one can consider the Br atoms to be (intrinsic) defects of a perfect $((CH_3)_4N)_2ZnCl_4$ crystal, although the number of these defects is then relatively large for a $((CH_3)_4N)_2ZnCl_{2.8}Br_{1.2}$ crystal. Nevertheless, one may get an idea, in this way, of the role played by defects in an incommensurately modulated crystal.

We have organized this paper as follows. First, the temperature dependence of the crystal structure of $((CH_3)_4N)_2ZnCl_{2.8}Br_{1.2}$ is described. After that, we describe the sample treatment and the most important details of the measuring method. Then, we discuss the interpretation of the HAUP data. Subsequently, the results are presented and discussed.

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TABLE I. Successive phase transitions in $((CH_3)_4N)_2ZnCl_{2.8}Br_{1.2}$. The structural data represent the case in which one disregards the difference between Br and Cl. The parameter γ determines the modulation wave vector according to the relation $\vec{q}=\gamma\vec{c}^*$.

Phase	V	IV	III	II	I
Temp (K)	$<223(=T_{c3})$	$<240(=T_{c2})$	$<280(=T_c)$	$<294(=T_i)$	$>294(=T_i)$
Symmetry	$P12_1/c1$		$P112_1/n$	$Pcmn(00\gamma)(1s\bar{1})$?	$Pcmn$
γ	1/2	1/3 and 1/2	1/3	$0.36-0.39$	0
System	Monocl.		Monocl.	Orthorh. ?	Orthorh.
Gyration tensor g	$\emptyset$		$\emptyset$	**?**	$\emptyset$
Indicatrix rotation	around b		around c	**?**	none

II. CRYSTAL STRUCTURE OF $((CH_3)_4N)_2ZnCl_{2.8}Br_{1.2}$ AS A FUNCTION OF TEMPERATURE

The x-T phase diagram of $((CH_3)_4N)_2ZnCl_{4-x}Br_x$ crystals was determined by Colla *et al.*[1] In Table I we present the successive phases that can be indentified if one disregards the difference between Cl and Br.

Phase I is a paraelastic phase with space group $Pcmn$ ($|a|=$ 15.67 Å, $|b|=$ 9.07 Å, and the pseudohexagonal axis $|c|=$ 12.39 Å). At T_i a phase transition into an incommensurate phase occurs. From our birefringence measurements we find the value $T_i=294$ K, which differs from the value $T_i=290$ K given by Colla *et al.*[2] The behavior of the modulation parameter γ in the incommensurate phase has been investigated by Vogels *et al.*[14,15] It was found that the modulation wave vector $\vec{q}$ locks at several commensurate values of γ in the incommensurate phases of $((CH_3)_4N)_2ZnCl_{4-x}Br_x$ crystals ($x>0$). The exact temperature behavior of γ can, however, differ from one crystal to another.[15] The locking behavior can also be considered from the point of view that the Br atoms are intrinsic defects. It was shown by Bziouet *et al.*[16] that a large (x-ray-induced) defect concentration in crystals of $((CH_3)_4N)_2ZnCl_4$ ($x=0$) also causes the modulation wave vector to lock at several rational values.

At $T_c=280$ K a lock-in phase transition into a ferroelastic phase takes place. The crystal has then a threefold superstructure and evolves into a multidomain state. Two other phase transitions are known to occur at lower temperatures. We have only performed measurements in phases I and II.

III. SAMPLES

Colorless crystals of about 1 cm^3 with large natural faces have been grown by means of a thermal convection method[17] from a stoichiometric aqueous solution of $((CH_3)_4N)$Hal and $ZnHal_2$ (Hal=Br,Cl) for the value $x=1$. The value of x for the crystals growing from such a solution is always somewhat larger,[18] being $x=1.2$ in this case. The directions of the crystallographic axes a, b, and c were determined with the help of an optical goniometer. Two crystal platelets, one parallel to the natural (001) face and another parallel to the (101) face, were cut with a wire saw. The faces of these platelets were polished with diamond paste down to 1 μm size. In Table II we give the optical parameters that determine the light propagation in these samples.

The (001) sample was chosen because the direction of light propagation is parallel to the modulation wave vector in such a sample. The (101) sample was selected because previous HAUP measurements on several members of the A_2BX_4 family have shown interesting and controversial results for this sample orientation.[8]

IV. MEASUREMENTS

The measurements presented in this paper were carried out with a HAUP apparatus built in our laboratory. A description of this apparatus has been given by Dijkstra *et al.*[11] Some essential improvements were made in this setup, which have been discussed by Kremers and Meekes.[12]

In case of the (001) sample measurements were performed as a function of the temperature for two different wavelengths $\lambda=632.8$ nm and $\lambda=500$ nm. The same sample was also subjected to measurements as a function of wavelength at two different temperatures $T=305$ K and $T=290$ K. The (101) sample was measured only as a function of temperature for the wavelength $\lambda=632.8$ nm. We want to point out that we have checked the obtained linear birefringences by measurements on two additional samples that were prepared with different thicknesses. In this way it is

TABLE II. The two samples that have been used in the present experiments and the optical parameters that are relevant. n_a, n_b, and n_c are the main refractive indices. The gyration tensor g and the unit wave vector $\vec{s}$ of the light determine the gyration G that is observed. The indices of G indicate the gyration tensor element that gives the largest contribution to the total gyration for the direction $\vec{s}$. The corresponding linear birefringence and other optical properties are labeled with the same indices.

Sample	Sample surface	Thickness (mm)	Linear birefringence Δn	Gyration $G=g_{ij}s_is_j$
1	(001)	1.80	$\Delta n_{33}=n_a-n_b$	$G_{33}=g_{33}$
2	(101)	2.05	$\Delta n_{13}\approx 0.62(n_a-n_b)+0.38(n_b-n_c)$	$G_{13}=0.39g_{11}+0.62g_{33}+0.97g_{13}$

possible to determine the value of the linear birefringence without doubt.

In the measurements as a function of temperature at least two extinction directions[12] were measured, in order to determine the rotation of the indicatrix with a large accuracy.[19] The temperature was left to stabilize for about half an hour after each change of its value, because we have learned from previous experiments that shorter stabilization times can lead to irreproducible results. It has been shown by Colla *et al.*[2] that the modulation wave vector has a larger tendency to lock at rational values of γ as the temperature is varied more slowly. In our case one can consider the temperature variation to be very slow in this respect.

V. INTERPRETATION OF THE MEASUREMENTS

The results presented in this paper were obtained with the interpretation that has been presented by Kremers and Meekes.[12] Both the so-called $\Delta\Theta$ correction and the ΔY correction were carried out. The latter reduces the magnitude of the δY error, typical in the HAUP method, to the order of 10^{-5} or smaller. The $\Delta\Theta$ correction improves all results, but is especially important for an accurate determination of the rotation of the optical indicatrix. Although the crystals of $((CH_3)_4N)_2ZnCl_{4-x}Br_x$ are totally transparent for visible light, we have taken the possible presence of small linear dichroism $\Delta\kappa$ into account. This effect may be caused by anisotropic surface scattering. The absolute value of of the linear dichroism $|\Delta\kappa|$ never exceeded 1×10^{-6}.

The optical properties of a sample that determine the propagation of light with unit wave vector $\vec{s}$ are extracted from the intensities measured in the HAUP experiment by fitting these intensities to the so-called HAUP intensity formula. In this way one finds the value of $4\sin^2(\pi z\Delta n/\lambda)$ from which the linear birefringence Δn has to be calculated (z is the thickness of the sample). From one of the fitting parameters one also obtains the value of

$$2\delta Y\cos^2(\pi z\Delta n/\lambda)-[(p-a)+2k]\sin(2\pi z\Delta n/\lambda), \quad (1)$$

where $k=G/(2\tilde{n}\Delta n)$ in which $\tilde{n}$ is the average refractive index and G is the gyration. The parameters p and a are the small parasitic ellipticities of the light polarized by, respectively, the polarizer and the analyzer. We have determined the value of the systematic error δY from expression (1) at that temperature or wavelength where $\sin(2\pi z\Delta n/\lambda)$ equals 0. The value of expression (1) is equal to $2\delta Y$ at such a point. Subsequently one can calculate the behavior of $(p-a)+2k$. The parameter $(p-a)$ gives a constant contribution to this behavior, which can only be determined if one is certain that k is equal to zero for part of the measurements. This is not the case for our measurements. However, it is well known from other experiments that $(p-a)$ has a magnitude in the order of 10^{-4}.[12,20] One can, therefore, estimate the gyration by neglecting $(p-a)$ in the case that the value of $(p-a)+2k$ is much larger than 10^{-4}.

Furthermore, the measurements provide the values of

$$\Theta_0=\tfrac{1}{2}(p+a)\cot(\pi z\Delta n/\lambda)-\tfrac{1}{2}\delta Y+\delta\Theta_{\text{indicatrix}}.$$

The parameter $\delta\Theta_{\text{indicatrix}}$ represents a possible rotation of the optical indicatrix. An equal contribution $\delta\Theta_{\text{indicatrix}}$ is found in the measurement of the other extinction direction, whereas Δn changes sign for the latter. By comparing the values of Θ_0 for both extinction directions and subtracting the corresponding contributions $\frac{1}{2}(p+a)\cot(\pi z\Delta n/\lambda)-\frac{1}{2}\delta Y$ it is possible to find the rotation of the optical indicatrix with a large accuracy.[19] In order to do this, however, the value of $p+a$, which does depend on the extinction direction, must be determined. We have done this by plotting Θ_0 against $\cot(\pi z\Delta n/\lambda)$ for a small part of the measurements where $\delta\Theta_{\text{indicatrix}}$ is (nearly) constant.

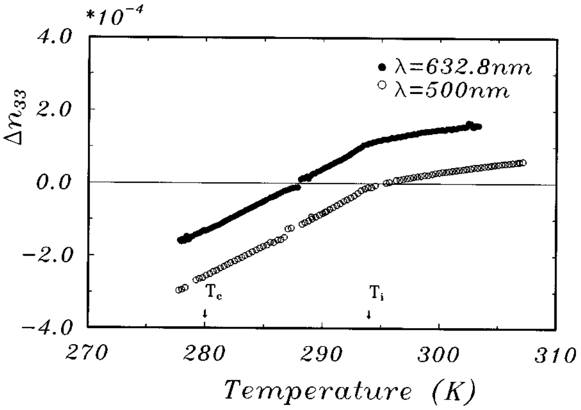

FIG. 1. The linear birefringence Δn_{33} of $((CH_3)_4N)_2ZnCl_{2.8}Br_{1.2}$ at two different wavelengths as a function of temperature in the paraelastic and incommensurate phases.

VI. RESULTS

A. Linear birefringence

The linear birefringence Δn_{33} of the (001) sample as a funtion of temperature has been plotted in Fig. 1. A clear change of slope is observed at $T_i=$ 294 K. This temperature is, therefore, believed to indicate a (second-order) phase transition. A straight line behavior of the linear birefringence is observed below T_i. The discontinuities are a result of the inaccuracy of the HAUP method in those cases that $\sin(\pi z\Delta n/\lambda)$ equals zero. The behavior of the linear birefringence as a function of wavelength is presented in Fig. 2. The lock-in phase transition at $T=T_c$ is faintly visible in the mea-

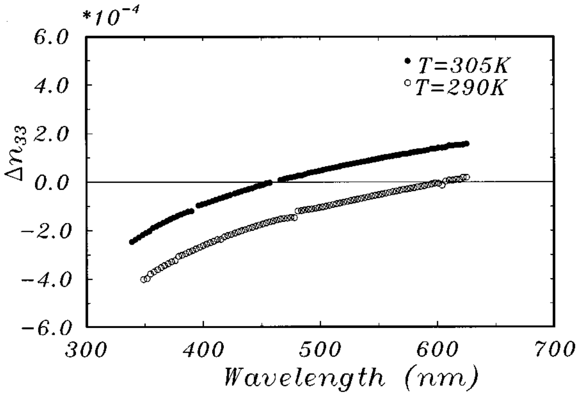

FIG. 2. The linear birefringence Δn_{33} of $((CH_3)_4N)_2ZnCl_{2.8}Br_{1.2}$ at two different temperatures as a function of the wavelength of the light.

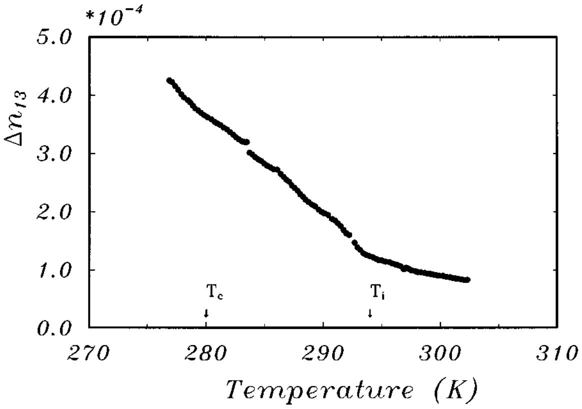

FIG. 3. The linear birefringence Δn_{13} of $((CH_3)_4N)_2ZnCl_{2.8}Br_{1.2}$ as a function of temperature. The wavelength of the light is $\lambda = 632.8$ nm.

surement at $\lambda = 632.8$ nm. The results of Figs. 1 and 2 agree nicely. We want to recall that the temperature dependence of Δn_{33} has been checked by measuring another (001) sample with a different thickness.

In Fig. 3 we present the linear birefringence Δn_{13} for the (101) sample as a function of the temperature. Also in this case we have checked the result by measurements on another (101) sample with a different thickness. Again a change of slope is observed at $T_i = 294$ K, but now also at approximately $T = 297$ K. In addition, the birefringences changes slope at several temperatures in the incommensurate phase, contrary to the results in Fig. 1. It is explained in the discussion that these deviations can be attributed to the behavior of the modulation wave vector with temperature.

Note, that compared to the case of $x = 0$ (Ref. 8) the behavior of Δn_{33}, as a function of temperature at $\lambda = 632.8$ nm is comparable, whereas the behavior of Δn_{13} is very different. Thus, in the latter case, a clear influence of the substitution of Cl for Br is observed.

B. Gyration

It has been explained in Sec. V that it is possible to determine the value of $(p-a)+2k$ from the measurements. The parameter k represents the ellipticity angle of the elliptical eigenpolarizations of the light that propagates in the sample. We have plotted in Fig. 4 the temperature dependence of $k+\frac{1}{2}(p-a)$ for the (001) sample and the two different wavelengths used. Note that $(p-a)$ is a constant with a magnitude in the order of 10^{-4}.[12,20] Therefore, it is clear that k, and consequently G_{33}, is nonzero already in the paraelastic phase. It has been explained in the Introduction that one can expect this, because the centrosymmetry is broken by the complete miscibility of Br and Cl. Crystals of $((CH_3)_4N)_2ZnCl_{4-x}Br_x$ are, therefore, indeed optically active. This gives the possibility of studying the influence of the presence of the modulation wave vector on a nonzero optical activity.

In Fig. 5 we show the the temperature dependence of $k+\frac{1}{2}(p-a)$ for the (101) sample. Also in this case there is nonzero optical activity both in the paraelastic and incommensurate phases. The ellipticity angle k, however, shows a remarkable behavior. Several plateaus of constant k are observed. We have drawn horizontal dashed line segments through these plateaus. Even above T_i a plateau is present. The origin of this remarkable behavior is addressed in the discussion.

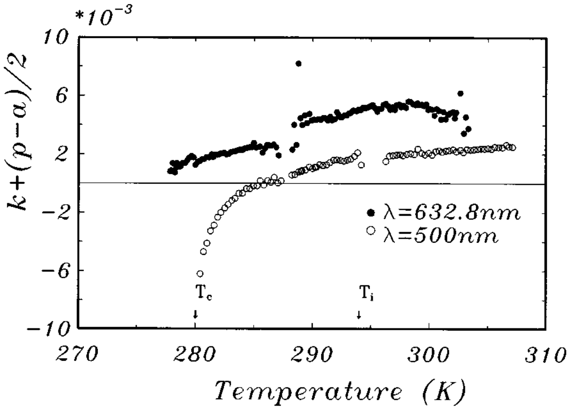

FIG. 4. The temperature dependence of $k+\frac{1}{2}(p-a)$ for the (001) sample at two different wavelengths.

The structure in the ellipticity angle k may be caused by the structure that is present in the linear birefringence, because of the relation $k = G/2\Delta n\tilde{n}$. In order to get an idea about the temperature dependence of the gyration G_{13}, we have neglected the contribution of $p-a$ in Fig. 5. For a first approximation this is reasonable, because the value of $p-a$ is small with respect to the observed values of $2k+(p-a)$. The circular birefringence $G_{13}/\tilde{n}$ can then be calculated. The results are presented in Fig. 6 which shows that the structure in k is not only due to the behavior of the linear birefringence. Also the gyration G_{13} shows a very characteristic behavior.

C. Rotation of the optical indicatrix

In Fig. 7 we have plotted the rotation of the optical indicatrix as derived for the (101) sample. In a truly orthorhombic crystal indicatrix rotation is forbidden by symmetry. The

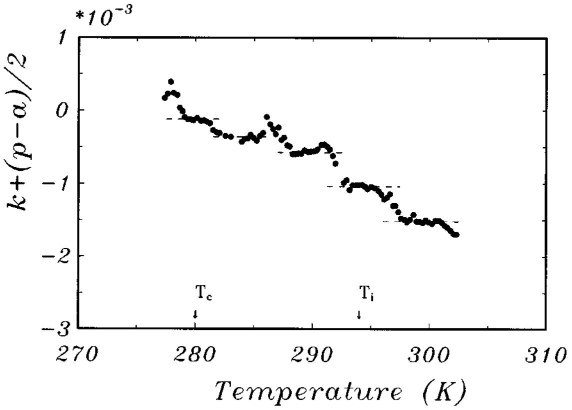

FIG. 5. The temperature dependence of $k+\frac{1}{2}(p-a)$ for the (101) sample. The dashed horizontal line segments have been drawn as a guide to the eye. The wavelength of the light is $\lambda = 632.8$ nm.

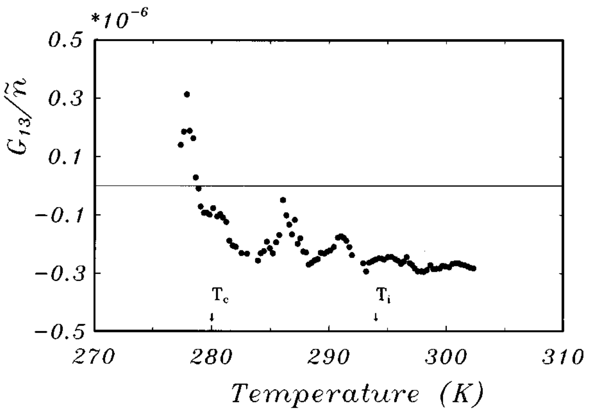

FIG. 6. The temperature dependence of the circular birefringence $G_{13}/\tilde{n}$, obtained by neglecting the contribution of $p-a$. The wavelength of the light is $\lambda=632.8$ nm.

nonconstant behavior in the paraelastic phase of $((CH_3)_4N)_2ZnCl_{2.8}Br_{1.2}$ again demonstrates the fact that a point group symmetry *mmm* is not present. In the incommensurate phase a rotation of approximately 2×10^{-3} rad is observed.

VII. DISCUSSION

From the measured birefringences Δn_{33} and Δn_{13} we have concluded that the phase transition from the paraelastic phase to the incommensurate phase occurs in $((CH_3)_4N)_2ZnCl_{2.8}Br_{1.2}$ crystals at the temperature $T_i=294$ K. Vogels *et al.*[14] observed satellite faces on the morphology of these crystals up to exactly the same temperature. The transition temperature derived by Colla *et al.*[2] from differential scanning calorimetry, on the other hand, was $T_i=290$ K. This difference may be caused by the fact that a much larger cooling rate was used by Colla *et al.*[2] Another reason may be found in the differences that are observed for different individual crystals. The birefringence Δn_{13} presented in Fig. 3, for example, shows several deviations from a straight line behavior in the incommensurate phase. In other samples, however, we did observe a perfectly linear dependence on temperature of the birefringence Δn_{13}. It is our opinion that the behavior of the modulation wave vector is very sensitive to the presence of defects in $((CH_3)_4N)_2ZnCl_{2.8}Br_{1.2}$ crystals, but more importantly that the behavior of the modulation wave vector clearly influences the optical properties. A strong indication for the latter is given by the results in Fig. 5. One observes five plateaus of more or less constant ellipticity angle k in this figure. In other $((CH_3)_4N)_2ZnCl_{2.8}Br_{1.2}$ samples having the same orientation, we also observed a clearly nonzero k, which has, however, a smooth temperature dependence without plateaus. The results in Fig. 5 are, nevertheless, very interesting.

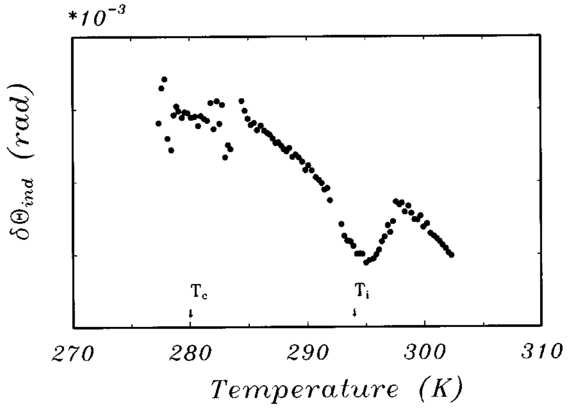

FIG. 7. Rotation of the optical indicatrix in the (101) sample for the wavelength $\lambda=632.8$ nm. The distance between the tick marks on the ordinate axis equals $1\cdot10^{-3}$. There is no absolute scale, because Θ_0 can only be measured with respect to an arbitrary origin.

As mentioned before, it is known that large defect concentrations can cause the modulation wave vector to lock at several commensurate values in $((CH_3)_4N)_2ZnCl_4$ crystals. Moreover, such a locking behavior seems to be a characteristic intrinsic property of $((CH_3)_4N)_2ZnCl_{4-x}Br_x$ crystals.[15] Therefore, we attribute the plateaus in Fig. 5 to regions of different commensurate modulation wave vectors. Note that this would imply that the modulation wave vector already has a certain temperature dependence above $T_i=294$ K. Whether the structure in the high-temperature phase indeed is due to a precursor effect of the modulation or due to a pinning effect of the possible disorder[21,22] by the intrinsic defects of the Cl and Br distributions over the zinc-halide tetrahedra is not clear. Presumably, the Cl and Br distributions and the actual modulation properties are intimately coupled, at least in the incommensurate phase. In any case, the structure in the high-temperature phase also effects the rotation of the optical indicatrix at $T\approx297$ K. It is striking that at the latter temperature the phase transition to the incommensurate phase occurs for $((CH_3)_4N)_2ZnCl_4$ $(x=0)$. At present we cannot say whether this is a coincidence. Another explanation for the observed plateaus might be found in the temperature dependence of the amplitude of the modulation. However, one only expects a steady increase of the amplitude with decreasing temperature. This cannot explain the observed behavior of k. Also the unit cell parameters of the average lattice are known to show a smooth temperature dependence.

Thus, we believe that in Fig. 5 one can, indirectly, observe a locking of $\vec{q}$ at different commensurate values. Between the plateaus the modulation wave vector may be incommensurate, changing continuously with temperature. It is also possible, however, that there are many different plateaus that are too small to be distinguished. Nevertheless, it is evident that the presence of the modulation influences the ellipticity angle k. The results presented in Fig. 6 demonstrate that also the optical activity is undoubtedly influenced by the presence of the modulation.

In the incommensurate phase the behavior of the rotation of the optical indicatrix resembles the behavior that was observed for $((CH_3)_4N)_2CuCl_4$.[9] It is interesting that this effect does not show plateaus in the incommensurate phase. It is possible that indicatrix rotation has a stronger dependence on the modulation amplitude than on the length of the modulation wave vector.

VIII. CONCLUSIONS

We have demonstrated that the difference between Cl and Br is essential for the optical properties of $((CH_3)_4N)_2ZnCl_{4-x}Br_x$ crystals. Due to the complete miscibility of Cl and Br the crystal cannot be considered to be orthorhombic, as has been proven by a nonzero indicatrix rotation in the paraelastic phase. Furthermore, the crystal cannot be considered to be centrosymmetric, as was proven by the measurement of nonzero optical activity in the paraelastic phase.

The measurements on a characteristic (101) sample have shown that the presence of the modulation wave vector has a definite influence on the birefringence, on the rotation of the optical indicatrix, and on the optical activity. The latter may provide an important impulse in the search for nonzero optical activity in the incommensurate phase of crystals that are not optically active in the high-temperature phase I.

It is our opinion that a more complete investigation of $((CH_3)_4N)_2ZnCl_{4-x}Br_x$ crystals with varying defect concentrations could be very fruitful if it were combined with the determination of the temperature dependence of the modulation by means of, for example, x-ray diffraction experiments.

ACKNOWLEDGMENTS

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