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A study of the mechanism of the ferroelectric transition in monoclinic K_2ZnBr_4

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Abstract. Structural investigations and dielectric measurements in the range from audio to microwave frequencies have been performed in order to reveal the static and dynamic nature of the ferroelectric transition of potassium tetrabromozincate. In the ferroelectric phase a tilt of the tetrabromozincate tetrahedra and a shift of the two independent potassium ions in the same direction constitute the main structural changes at the transition and account almost quantitatively for the observed spontaneous polarization. In the paraelectric region two bromine atoms of each tetrahedron are disordered. They are assumed to move in double wells and to be responsible for the Debye-like dielectric relaxation that was found in the microwave region. The potassium ions and the other two bromine atoms are much less disordered, if at all, but contribute substantially to the condensing mode of A_u symmetry. The characteristic frequencies of these latter atoms are beyond 10 GHz. The transition may be classified as partially order–disorder and partially displacive.

1. Introduction

Potassium tetrabromozincate is known to exist at ambient temperature in a stable monoclinic modification with the Sr_2GeS_4 -type structure and two formula units per unit cell. It undergoes a ferroelectric transition at a temperature $T_c \simeq 155$ K, where the space group changes from $P12_1/m1$ to $P12_11$ (Shimizu *et al* 1990, Kasano *et al* 1992, Fábry *et al* 1993). It transforms to another, metastable orthorhombic modification with the β - K_2SO_4 -type structure when crystals are heated to above 450 K (Shimizu *et al* 1990, Mashiyama *et al* 1991). The latter modification displays a very different sequence of transitions, which resembles those of other A_2BX_4 -type crystals such as Rb_2ZnCl_4 and will not be dealt with in this paper. The crystal structures of monoclinic K_2ZnBr_4 (henceforth abbreviated as KZB) in its paraelectric and ferroelectric phases have been solved by Kasano *et al* (1992) and Bärnighausen (1992) by x-ray diffraction studies. Their results show that the high-temperature phase is partially disordered with respect to the tetrabromozincate tetrahedra and that in the ferroelectric low-temperature phase the tetrahedra are ordered and the two inequivalent potassium ions are shifted in the same direction almost parallel to the polar b -axis.

The purpose of the present paper is to reveal the characteristic features of the ferroelectric transition in KZB with respect to its static and dynamic nature. Therefore, an analysis of structure determinations, of quasistatic dielectric investigations, and of detailed measurements of the dielectric dispersion in the microwave region will be presented. Although the results on the crystal structures of KZB as mentioned above agree in the main, they differ in some important details, which turned out to be essential for the interpretation of the transition mechanism.

2. Experimental results

2.1. Sample preparation and experimental methods

The structural studies were done on tiny crystals ($0.03 \times 0.05 \times 0.06 \text{ mm}^3$) grown in a supersaturated aqueous solution of stoichiometric amounts of KBr and ZnBr_2 at about 378 K. For protection against moisture the crystals were sealed in Mark capillaries under dry Ar.

Large single crystals for the dielectric measurements were grown in aqueous solutions at about 380 K by slow evaporation (Shimizu *et al* 1990) and recrystallized twice. The solutions were prepared from KBr and ZnBr_2 with a molar ratio of 2:1.5. They were colourless at the beginning of the crystal-growing period of about one month and became slightly yellowish due to bromine at the end. The crystals, with linear dimensions of 1–2 cm, were colourless and very deliquescent in air when the relative humidity exceeded some 30%. Rectangular plates or cylindrical discs were cut perpendicular to the *b*-axis; the surfaces were covered with sputtered Au electrodes. Typical samples had an area between 10 and 20 mm² and a thickness between 0.5 and 1 mm. Quantitative results turned out to depend strongly on the preparation, i.e. on the surface layer of hydrates that could form during the manipulations at the air. Therefore, samples were prepared under paraffin oil or in a dry atmosphere as much as possible and surrounded by dry He gas during the measurements.

Single-crystal structure determinations were performed at four different temperatures (128, 173, 206 and 295 K) by means of an automated STOE four-circle x-ray diffractometer and graphite-monochromated Mo K_α radiation. About 1450 independent reflections have been used, carefully corrected for absorption effects. Least-squares refinements were done with 41 and 64 free parameters above and below the Curie temperature, respectively, and led to R_w values between 1.35% (128 K) and 2.59% (295 K). The 128 K parameter set was refined with regard to twin domains. In addition, temperature-dependent measurements of the lattice constants were carried out in the range between 113 and 295 K, and the phase transition has been studied in greater detail around T_c by means of about 120 specific reflections strongly influenced by the transformation. Temperatures are estimated to be correct within ± 1.5 K.

Dielectric investigations at low frequencies (10 kHz–1 MHz) were done by an automated LCR meter (hp 4275A) and at measuring-field strengths of about 2 V cm^{-1} . The temperature rate at continuous measurements of the permittivity was 1.5 K min^{-1} in general and 0.4 K min^{-1} in the vicinity of the transition. Hysteresis loops were recorded by the usual Sawyer–Tower circuit and a digital storage oscilloscope. Measurements of the dielectric dispersion at high frequencies (1 MHz–10 GHz) were performed by means of a coaxial reflectometer set-up using complex network analysers (hp 4191 and hp 8510B). Here the cylindrical samples fill the central section of a radial transmission line, which forms the termination of the coaxial sample holder (Luther 1973). The frequency dependence of the complex permittivity was measured at respective constant temperatures, the variations of which were less than ± 0.01 K. Temperatures have been measured by an Si diode or Pt resistance thermometer. Absolute values are correct within ± 0.5 K.

2.2. Structural investigations

The lattice dimensions and positional parameters for one temperature above T_c (173 K) and one below T_c (128 K) are given in table 1. The results are in general agreement with those of Kasano *et al* (1992) but the accuracy is about four times better with respect to

Table 1. Crystal structure of K_2ZnBr_4 at (i) 128 K, space group $P12_11$, and (ii) 173 K, space group $P12_1/m1$. Top, lattice dimensions in ångströms, angle β in degrees; bottom, positional parameters of the atoms. Standard deviations are in parentheses.

	<i>a</i>		<i>b</i>		<i>c</i>		β	
	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
	9.012(2)	9.077(2)	7.431(2)	7.436(2)	7.223(2)	7.208(2)	108.76(2)	108.86(2)
Atom	<i>x</i>		<i>y</i>		<i>z</i>			
	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
K(1)	0.048 69(9)	0.046 83(9)	0.228 65(14)	0.25	0.710 34(13)	0.707 74(13)		
K(2)	0.571 60(9)	0.572 90(9)	0.227 98(14)	0.25	0.774 23(13)	0.776 32(13)		
Zn	0.204 33(4)	0.205 31(4)	0.25 (fixed)	0.25	0.279 90(6)	0.280 70(6)		
Br(1)	-0.070 53(4)	-0.068 59(4)	0.271 07(9)	0.25	0.100 43(6)	0.103 72(7)		
Br(2)	0.369 19(4)	0.367 27(4)	0.265 28(10)	0.25	0.078 37(6)	0.077 41(6)		
Br(3)	0.259 49(5)	0.265 44(3)	-0.011 97(9)	-0.002 61(3)	0.486 37(6)	0.501 97(4)		
Br(4)	0.268 61(5)	[0.265 44(3)]	0.493 10(8)	[0.502 61(3)]	0.514 89(6)	[0.501 97(4)]		

the standard deviations. A comparison of the structures at 173 and 128 K reveals that a cooperative tilt of the (distorted) tetrabromozincate tetrahedra around an axis almost parallel to the *a*-axis and a shift of the two independent K^+ ions almost along the *b*-axis constitute the main contributions of the structural changes through the transition (figure 1). At the same time the coordination number of both K^+ ions increases from six to seven. As both K^+ ions are shifted in the same direction with respect to the centre of mass of the $ZnBr_4^{2-}$ ion, these shifts are essential for the degree of polarity of the ferroelectric phase.

The positional disorder of the atoms within the paraelectric phase may be estimated from the anisotropic temperature factors, which are known from the structure determinations. The corresponding mean-square displacements (MSDs) are plotted for all the atoms in figure 2 versus temperature, and the linear temperature dependences of the respective maximal MSDs, which were determined at temperatures above T_c , are extrapolated to 0 K. Anomalous MSDs are seen for Br(1), Br(2) and to a lesser degree for K(1) and K(2). A striking agreement has to be noted between the MSD values of Br(1) and Br(2) extrapolated to 0 K and converted into finite positional shifts Δy on one hand ($\Delta y = 0.021$ and 0.018 , respectively) and the corresponding shifts of Br(1) and Br(2) measured in the ferroelectric phase on the other (see table 1). A similar statement holds neither for K(1) and K(2) nor for Br(3) and Br(4), although these atoms undergo shifts comparable to those of Br(1) and Br(2) when the crystal passes the transition.

Figure 3 displays the temperature dependence of the lattice parameters in relation to their respective values at 295 K. It is noticed that all the parameters vary continuously at T_c within the experimental resolution of about 2×10^{-4} . This indicates that the transition is of second order. The values of each parameter measured above T_c have been fitted to a polynomial of second degree in T and the curves obtained have been extrapolated to the ferroelectric region. It is striking that the monoclinic angle β and the cell volume V follow this extrapolation at least down to about 120 K. Fitting the parameters $a_r(T)$, $b_r(T)$ and $c_r(T)$ for $T < T_c$ in a corresponding manner the intersections of the two respective fit curves led to transition temperatures of (158 ± 1) K in agreement with the dielectric investigations, the description of which follows.

2.3. Low-frequency dielectric measurements

The complex relative permittivity $\epsilon^* = \epsilon' - i\epsilon''$ has been measured at low frequencies in

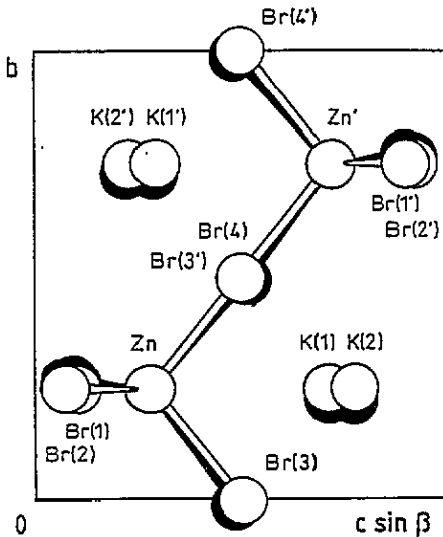


Figure 1. Projections of the unit cell of KZB along the a -axis at 173 K (open circles) and at 128 K (full circles). The latter represents the structure of one of the two possible transformation twin individuals, which are related by the lost mirror plane at $b/4$.

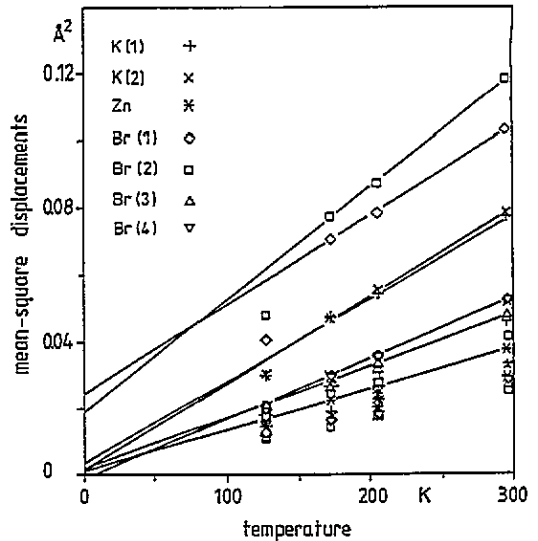


Figure 2. MSDs of atoms as a function of temperature. The straight lines extrapolate the behaviour of the respective largest MSDs of each atom in the paraelectric phase to 0 K.

the temperature range between 100 and 300 K. The real part ϵ' obeys a Curie–Weiss law

$$\epsilon' = \epsilon_{\infty} + C/(T - T_0) \quad (1)$$

in the remarkably wide range from the transition up to ambient temperature, where $\epsilon_{\infty} \simeq 8.1$, $C \simeq 3100$ K and $T_0 \simeq 155.2$ K. Among samples cut from three different single crystals the parameter C varied by $\pm 9\%$, ϵ_{∞} by $\pm 7\%$, and T_0 by ± 0.9 K, whereas the temperature of maximal permittivity, $T_c = (155.85 \pm 0.15)$ K, was very well reproducible. For these samples the maximal values of $\epsilon'(T_c)$ on cooling runs ranged between $\epsilon_{\max} = 2 \times 10^3$ and 3.5×10^4 at a frequency of 10 kHz, and in each case ϵ_{\max} was about 10% less on a subsequent heating run. The loss tangent amounted generally to less than 0.05 at T_c . These results point to a high quality of the bulk of our crystals, if we assume that the differences of ϵ_{\max} result from slightly different surface layers. An example of the Curie–Weiss behaviour is depicted in figure 4. The dielectric behaviour below T_c is widely determined by ferroelectric domains and will be referred to in section 2.4 together with the inset of figure 4.

Kasano *et al* (1992) consider the transition to be first order because of a small thermal hysteresis of less than 1 K, found by calorimetric and dielectric measurements (Shimizu *et al* 1990). From the dielectric results we infer that the transition is second order, as the temperature difference of ϵ_{\max} peaks between heating and cooling runs of our best samples was less than 0.04 K. No appreciable dielectric dispersion was noticed above T_c up to 1 MHz.

In order to compare the spontaneous polarization P_s of KZB with the dipole moment of the unit cell, which may be evaluated from the structural parameters, we decided to also remeasure P_s . Here again the surface layers due to hydration of the samples turned out to influence the results strongly. The repolarization in an external field is hindered by the

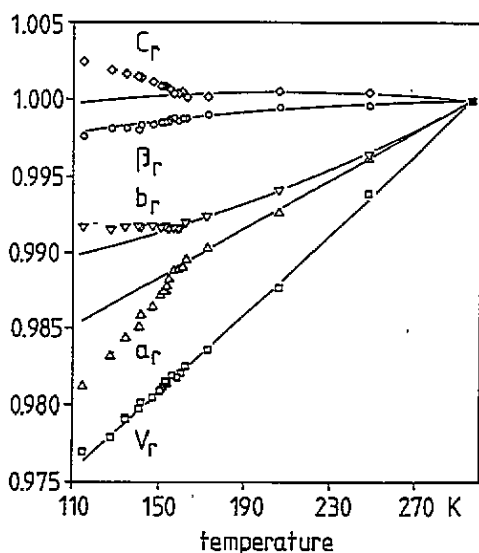


Figure 3. The variation of the geometrical parameters of the unit cell of KZB with temperature. Lattice dimensions a_r , b_r and c_r , monoclinic angle β_r , and cell volume V_r are normalized by their respective values at 295 K, $a = 9.166 \text{ \AA}$, $b = 7.493 \text{ \AA}$, $c = 7.207 \text{ \AA}$, $\beta = 108.96^\circ$, $V = 468.13 \text{ \AA}^3$.

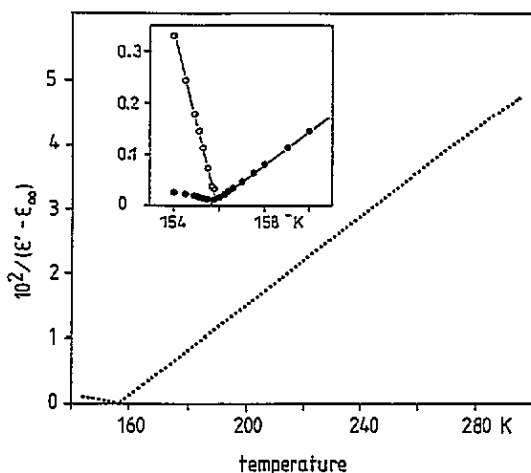


Figure 4. The Curie-Weiss behaviour of the quasistatic relative permittivity ϵ' at a frequency of 10 kHz with $\epsilon_\infty = 8.2$. The inset displays details around T_c measured on another sample with the high-frequency equipment. Full symbols represent the permittivity at the low-frequency side of the observed dispersion in the microwave region; open symbols refer to the permittivity when domain effects are excluded (see section 2.4).

dielectrically hard layers and if any, very slanted hysteresis loops result generally. The latter fact may be ascribed to the inhomogeneity of the layers. Therefore, samples with high values of $\epsilon'(T_c)$ were selected in order to have minimal layers and to obtain loops with steep slopes. The temperature dependence of P_s of two different samples is plotted in figure 5 together with typical loops. Although we find $P_s(100 \text{ K}) \simeq 2.7 \mu\text{C cm}^{-2}$, which is rather large compared with the $0.5 \mu\text{C cm}^{-2}$ found by Shimizu *et al* (1990) at the same temperature, we are not sure that the crystals are fully repolarizable at this temperature. In the neighbourhood of T_c , however, the dielectric saturation of well prepared samples was independent of the applied field strength and considered to be sufficient for a quantitative determination of P_s . The hysteresis loops were taken without any compensation for electric losses and their curvilinear parts of saturation have been extrapolated to zero field strength in order to read P_s . The estimated error of $\pm 5\%$ is mainly due to the uncertainty of this extrapolation. However, in the whole investigated temperature range a simple power law

$$P_s = p\{(T_c - T)/T_c\}^{\beta'} \quad (2)$$

could be fitted to the data of figure 5, where $p = (3.6 \pm 0.1) \mu\text{C cm}^{-2}$, $T_c = (155.9 \pm 0.2) \text{ K}$ and $\beta' = 0.26 \pm 0.01$. Double hysteresis loops, which appear typically slightly above the transition temperature of a first-order transition, have not been observed. This points to a second-order transition, too.

Obviously, the apparent coercive field E_c may be influenced by a surface layer even more than P_s , as only a part of the applied external field drops across the bulk of the

samples. It should be noted, however, that KZB has rather low values of E_c , i.e. presumably one order of magnitude less than other order-disorder-type ferroelectrics such as triglycine sulphate.

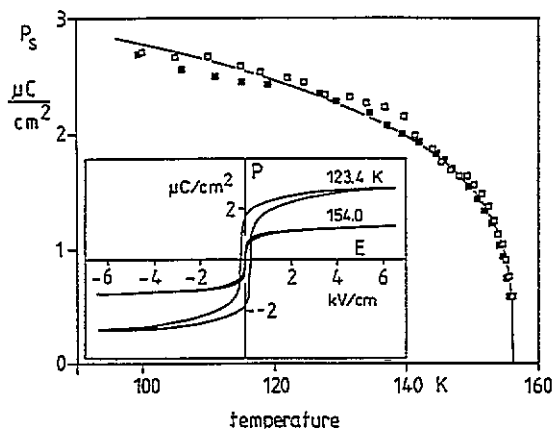


Figure 5. The temperature dependence of the spontaneous polarization of KZB measured on two samples from different single crystals. The inset displays typical hysteresis loops.

2.4. High-frequency dielectric measurements

Samples that had been exposed to humid air during the preparation and, therefore, had ϵ_{\max} values of less than about 1000, exhibited generally a dielectric dispersion in the frequency range of our high-frequency measurements. In most cases this could be observed from ambient temperature to below T_c . However, this dispersion, the characteristic frequency of which varied strongly between different samples, was absent when surface layers were avoided and will not be considered here.

A dispersion from the bulk has been detected only on well prepared samples with ϵ_{\max} values above about 3000 and in a relatively small temperature range from about 160 to 154 K. Cole-Cole plots for three temperatures above T_c and for two temperatures below T_c are displayed in the upper and lower parts of figure 6, respectively. The measurements have been evaluated by least-squares fits to the generalized Cole-Cole formula

$$\epsilon^* = \epsilon_h + \sum_{j=1}^n \frac{\Delta\epsilon_j}{1 + (i\omega\tau_j)^{1-h_j}} \quad (3)$$

where $n = 1$ was adequate above T_c and $n = 2$ in the ferroelectric region. The dispersion within the paraelectric region has a very small distribution parameter, $h_1 < 0.02$, and may be considered a simple Debye-type relaxation. It continues below T_c as a relatively weak dispersion at the high-frequency side of another strong dispersion, which appears right at the transition temperature. The characteristic frequency $f_2 = 1/(2\pi\tau_2)$ of the latter one coincides with that of the former one, $f_1 = 1/(2\pi\tau_1)$, at T_c , and it is practically impossible to separate the two relaxations in an interval of $T_c \pm 0.1$ K. The frequency f_1 has a minimal value at T_c and increases below T_c , whereas f_2 continues to decrease with decreasing temperature. The second dispersion with the frequency f_2 exhibits the

characteristic features of a relaxation of ferroelectric domain walls. Therefore, the value of the permittivity at the low-frequency side of the high-frequency relaxation, $\epsilon'_{1s} = \epsilon_h + \Delta\epsilon_1$, is ascribed to the (clamped, adiabatic) permittivity of the crystal below T_c without domains. Above T_c it coincides with the quasistatic permittivity ϵ' of equation (1). The temperature dependence of $1/\epsilon'_{1s}$ is plotted in the inset of figure 4 (open points). The dependence of the relaxation frequencies on temperature is depicted in figure 7. The frequency f_1 follows a Curie–Weiss-type law in a small temperature range below as well as above T_c , and the ratio of the respective slopes amounts to about -4.2 . Reliable measurements could not yet be performed outside the range between 154 and 160 K due to the frequency limits of the experimental set-up.

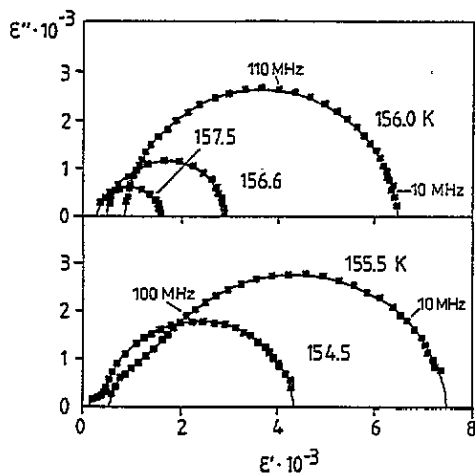


Figure 6. Cole–Cole plots of the complex permittivity at temperatures above (top) and below (bottom) the transition temperature $T_c \approx 155.7$ K.

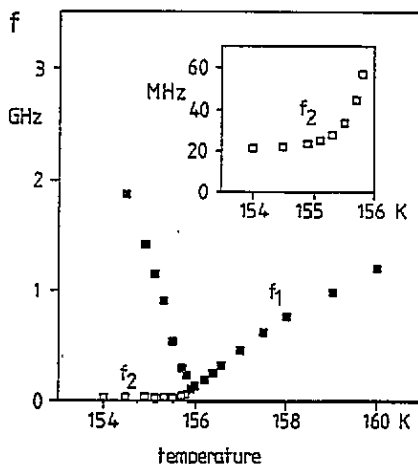


Figure 7. The temperature dependence of the relaxation frequencies of KZB in the vicinity of T_c . The inset displays the characteristic frequency f_2 of the domain-wall relaxation in greater detail.

A peculiarity of the measured dispersions are the anomalously high values of the permittivity ϵ_h , which according to equation (3) result when the Cole–Cole plots are extrapolated to infinite frequency. Indeed, ϵ_h has a maximal value of about 1000 at T_c (figure 8) and the temperature dependence of ϵ_h^{-1} resembles that of f_1 very much (compare figure 7). On the other hand, the Curie–Weiss behaviour of the static permittivity led to a temperature-independent value of $\epsilon_{\infty} \simeq 8.1$. Therefore, another dispersion at frequencies beyond 10 GHz must exist, the low-frequency permittivity of which is ϵ_h . The temperature dependence of ϵ_h has to be taken as an indication that this speculative dispersion is relevant to the ferroelectric transition of KZB, too.

3. Discussion

The experimental results confirm that monoclinic KZB undergoes an equitranslational, proper ferroelectric transition accompanied by a change of symmetry from $P12_1/m1$ to $P12_11$. This transition is of second order within the experimental accuracy. Therefore, the order parameter should transform according to a basis function of the irreducible representation

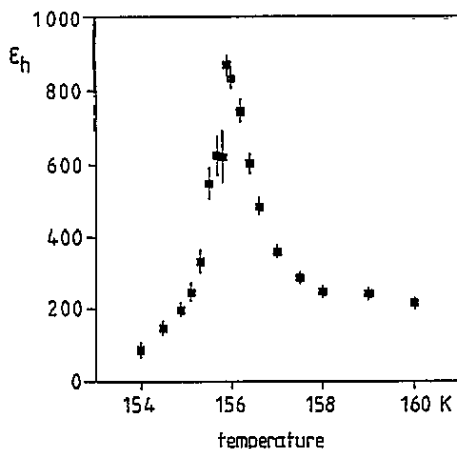


Figure 8. The temperature dependence of the real permittivity ϵ_h as obtained by extrapolating the Cole-Cole plots to infinite frequency (compare figure 6).

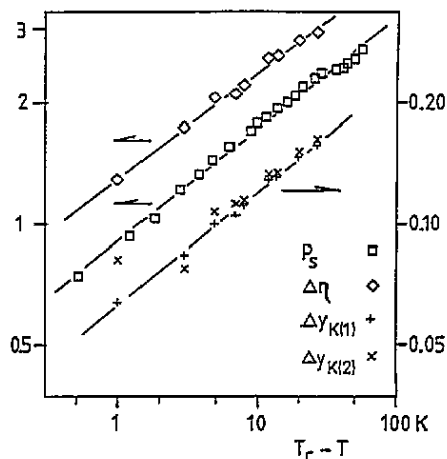


Figure 9. Double-logarithmic plots of the spontaneous polarization P_s (in $\mu\text{C cm}^{-2}$), of the displacements $\Delta y_{K(1)}$ and $\Delta y_{K(2)}$ (in \AA), and of the tilt angle $\Delta\eta$ of the tetrabromozincate ion (in degrees) versus $T_c - T$. The values of T_c have been determined separately for each quantity by a least-squares fit because of small differences between thermometers used.

A_h of symmetry class $2/m$, that is, according to the y-component of any vectorial property such as, e.g., the dielectric polarization.

Applying a point-charge model it is easy to evaluate the spontaneous polarization at 128 K from the positional parameters given in table 1 by the expression

$$P_s = \frac{2b}{V_z} \sum_{i=1}^7 q_i (y_i - y_{Zn}) \quad (4)$$

where i numbers the atoms of one formula unit. With the lattice parameter b and the cell volume V_z determined at 128 K, and ionic charges of $2e$ for Zn and of e and $-e$ for K and Br, respectively, equation (4) leads to $P_s = 3.16 \mu\text{C cm}^{-2}$. This value certainly represents an upper limit for P_s as neither covalent parts of the Zn-Br bonds nor the polarizabilities of the ions have been considered. Distributing the negative charge of the tetrabromozincate ion in such a way that each Br has a charge of $-e/2$, equation (4) gives $P_s = 2.71 \mu\text{C cm}^{-2}$. With respect to the simple model and to the experimental problems, the value of $2.4 \mu\text{C cm}^{-2}$ measured at 128 K agrees reasonably well with the calculated ones.

The temperature dependence of the order parameter may be established from the behaviour of $P_s(T)$ as well as from the temperature dependence of structural properties such as the antidistortive tilts of tetrabromozincate ions (cf figure 1). Assuming a tilt axis [100] the tilt angle $\Delta\eta$ can be evaluated to a first approximation from

$$\tan \Delta\eta = \frac{z_{\text{Br}(4)} - z_{\text{Br}(3)}}{y_{\text{Br}(4)} - y_{\text{Br}(3)}} \frac{c \sin \beta}{b}. \quad (5)$$

The double-logarithmic plots of $P_s(T_c - T)$ and $\Delta\eta(T_c - T)$ are displayed in figure 9 and show the analogous behaviour of these quantities. It is noticed that the same holds true for the translational shifts Δy of K(1) and K(2). From the slope of these linear dependences we evaluated a critical exponent of the order parameter of $\beta' = 0.27 \pm 0.02$.

A phenomenological interpretation of a critical exponent $\beta' = 0.25$ in the framework of Landau theory seems possible under the assumption that in the expression of the free enthalpy density

$$G = G_0 + \frac{1}{2}a_0(T - T_0)P^2 + \frac{1}{4}BP^4 + \frac{1}{6}CP^6 - EP \quad (6)$$

the fourth-order term may be neglected against the sixth-order one. Then, from equation (6) together with the condition of equilibrium, $\partial G/\partial P = 0$, follows (Grindlay 1970)

$$P(T < T_0) = [a_0(T_0 - T)/C]^{1/4} \quad (7)$$

$$R = (\partial E/\partial P)_{T < T_0}/(\partial E/\partial P)_{T > T_0} = -4. \quad (8)$$

This description implies that the system is at or very near to a tricritical point at ambient pressure. Relation (8) does not agree quantitatively with the observed value of -5.2 for the ratio of the slopes of the inverse permittivities below and above T_c . This ratio has been evaluated from the inset in figure 4, considering the permittivity of the homogeneous, i.e. domain-free crystal. However, as pointed out in section 2.4 the experimental values of $1/\epsilon'_{1s}$ refer to the clamped crystal in the piezoelectric low-temperature phase. Furthermore, the dielectric measurements were performed under adiabatic conditions. The mechanically free, isothermal values of the inverse permittivity are related to the measured ones by thermodynamic expressions, which may lead to a substantial increase of the modulus of R as has been shown for triglycine sulphate (TGS) by Luther (1973). Unfortunately, a similar evaluation cannot be done in our case as most of the material constants needed are unknown for KZB.

Although *static* properties of the ferroelectric phase are seen to be similar on a microscopic and a macroscopic scale, there exist distinct differences of the *dynamic* behaviour within the structure. The most striking feature is deduced from the temperature dependence of the MSDs of atoms (figure 2). The anomalous large MSDs of Br(1) and Br(2), which appear along the b -axis in the paraelectric phase, have to be interpreted as disorder in agreement with the analysis of Kasano *et al* (1992). These two Br ions are assumed to move in double wells, therefore, and to be responsible for the dielectric relaxation measured below 10 GHz in the vicinity of T_c . The other two Br ions are certainly not disordered and must be assumed to move independently. As a consequence the tetrahedra cannot be considered to move as rigid entities in the paraelectric phase, not even in a first approximation.

Remarkably large MSDs parallel to the b -axis are also observed for the K ions, but these values extrapolate nearly to zero at 0 K and hence a disorder of these ions cannot be inferred. However, the large fluctuations of K(1) and K(2) along the b -axis may be correlated in a natural way with the high values of the permittivity ϵ_h measured on the high-frequency side of the relaxation of Br(1) and Br(2). The corresponding vibrations of the K ions represent another branch of the soft mode of the system and must even be considered to trigger the transition, as the static permittivity relevant to this mode, ϵ_h , exhibits a strong temperature dependence and a pronounced maximum at T_c (figure 8).

The atomic displacements discussed above are symmetrically equivalent, i.e. transform according to the active irreducible representation A_u . Therefore, they are linearly coupling A_u -type symmetry coordinates, but with different dynamic properties. The mechanism of the ferroelectric transition of KZB may be described, therefore, as follows. The soft mode includes contributions from two symmetry coordinates, which are symmetrically equivalent and freeze out independently of their characteristic time scales in the ferroelectric phase. Accordingly the condensate displays contributions from the ordering process of Br(1) and

Br(2) and from the displacive shifts of K(1) and K(2) and it even incorporates relatively strong contributions from hard modes. The latter is shown by comparably large static displacements of Br(3) and Br(4), atoms that do not exhibit anomalous temperature factors above T_c .

Preliminary Raman spectroscopic investigations have also been performed. A soft mode, which should be Raman active in the polar phase, has not been detected. An analysis of the Raman spectra will be presented in a forthcoming paper.

Acknowledgments

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