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Linear birefringence anomalies in a $(CH_3NH_3)_5Bi_2Cl_{11}$ crystal

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Abstract. Linear birefringence measurements on a MAPCB crystal which revealed small increments in the temperature range 120–180 K are presented. Anomalies in the dielectric permittivity, polarization and specific heat have also been observed in similar temperature regions. These anomalies are regarded as possible evidence of the overcritical behaviour at the isomorphic phase transition. Linear birefringence increments and temperature derivatives of the linear birefringence caused by this transition are described and compared with the polarization and the specific-heat anomalies.

1. Introduction

$(CH_3NH_3)_5Bi_2Cl_{11}$ (MAPCH) belongs to a subfamily of alkylammonium halogenobismuthates(III), which exhibit many structural phase transitions [1].

The structure of the crystals is built up of discrete undecachlorodibismuthate anions and methylammonium cations [2]. An ordering of $(CH_3NH_3)^+$ cations leads to a specific sequence of phases in the crystal. At about $T_{c1} = 307$ K the MAPCB crystal undergoes a ferroelectric phase transition from the space group $Pcab$ to $Pca2_1$; P_S is directed along the c axis. Dielectric [3–5] and heat capacity anomalies [6–8] connected with a probable second phase transition were observed at about 160–170 K for MAPCB and at about 77 K for MAPBB. However, there were indications that the dielectric permittivity and specific-heat anomalies of MAPCB at about 170 K could be explained by the Landau-type free energy with an eighth-order term in polarization included [8, 9]. An overcritical behaviour near the isomorphic phase transition was assumed by Strukov *et al* [6]. Linear birefringence data for the MAPCB crystal in a wide temperature range were published recently [10].

A saturation effect below about 45 K and an anomalous behaviour of $\Delta(\Delta n_c)$ and $d(\Delta n_b)/dT$ at around 160 K were pointed out.

The aim of this paper is to present and describe the linear birefringence anomalies at around 160–170 K in a more detailed way.

2. Experimental details and results

The crystals were obtained by slow evaporation at a constant temperature of 290 K by R Jakubas (University of Wrocław). Refractive indices were evaluated by the prism minimum-deviation method [11]: $n_a = 1.643$, $n_b = 1.627$ and $n_c = 1.646(\pm 0.06)$ for MAPCB. The linear birefringence was measured using the rotating-analyser modulation method [12] in the temperature range 120–340 K. The accuracy of the method seems to be better than 10^{-6}. A He–Ne laser ($\chi = 632.8$ nm) served as a light source. The cooling and heating rates used in the phase transition region were 0.05 K min^{-1}, and the temperature was reliably determined at this rate of scan. As the crystal is orthorhombic, the optical cuts are the crystallographic cuts also.

The temperature dependences of the linear birefringence changes $|\Delta(\Delta n_a)|$ and $|\Delta(\Delta n_b)|$ and increments $|\delta(\Delta n_a)|$ and $|\delta(\Delta n_b)|$ in the temperature range 120–320 K are shown in figure 1 ($\Delta n_a = n_b - n_c$; $\Delta n_b = n_c - n_a$; $\Delta n_c = n_a - n_b$).

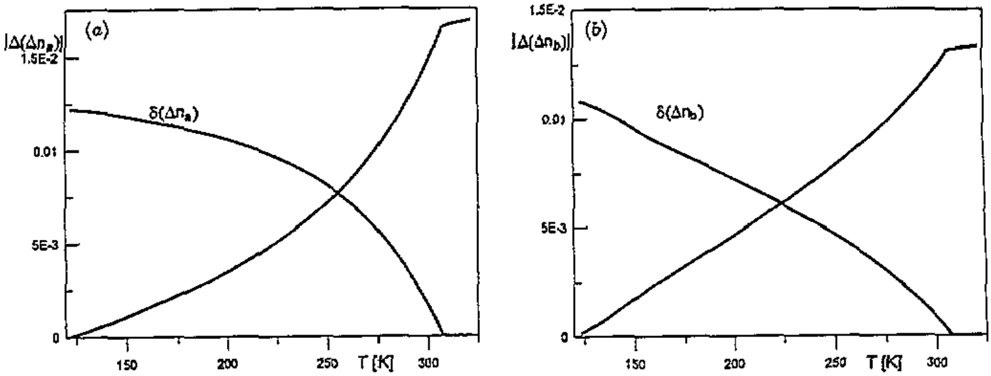

Figure 1. Temperature dependence of the linear birefringence changes and increments in the MAPCB crystal: (a) $|\Delta(\Delta n_a)|$ and $|\delta(\Delta n_a)|$ for the a cut; (b) $|\Delta(\Delta n_b)|$ and $|\delta(\Delta n_b)|$ for the b cut.

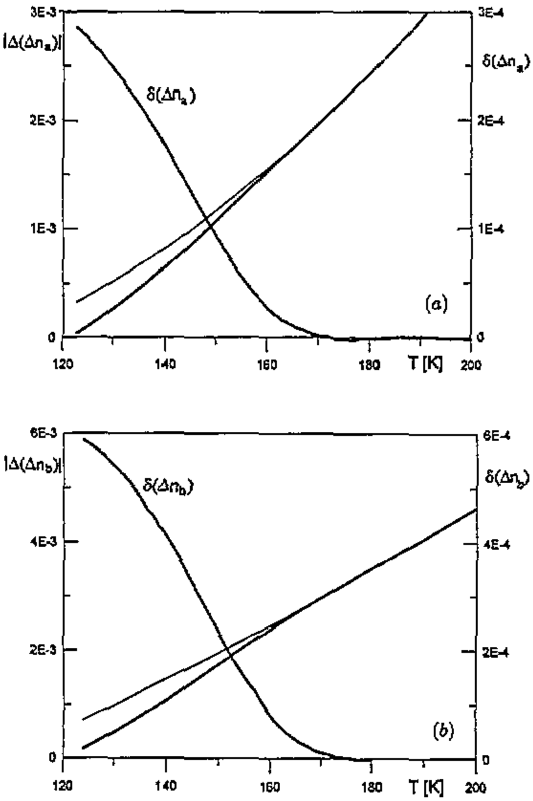

Figure 2. *Magnified parts of the linear birefringence changes starting at about 170 K for (a) the a cut and (b) the b cut. The extrapolated higher-temperature transients of $|\Delta(\Delta n_i)|$ are shown as thin lines. The temperature dependences of the linear birefringence increments $|\delta(\Delta n_a)|$ and $|\delta(\Delta n_b)|$ below 170 K are also shown.*

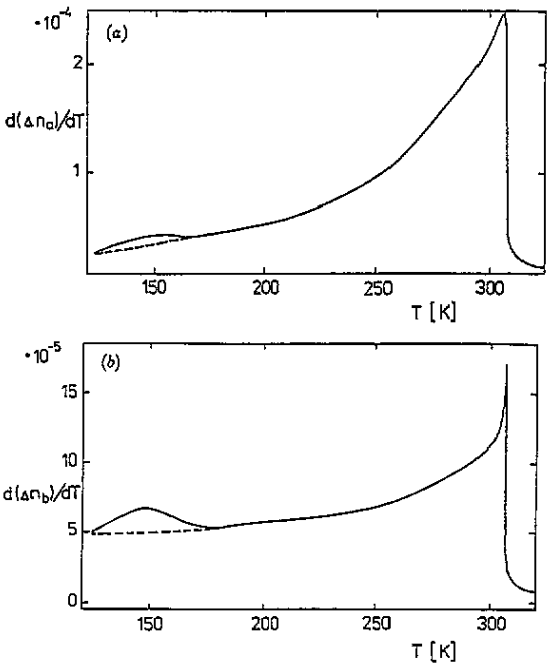

Figure 3. Temperature derivatives $d(\Delta n_i)/dT$ of the linear birefringence as functions of temperature for (a) the *a* cut and (b) the *b* cut.

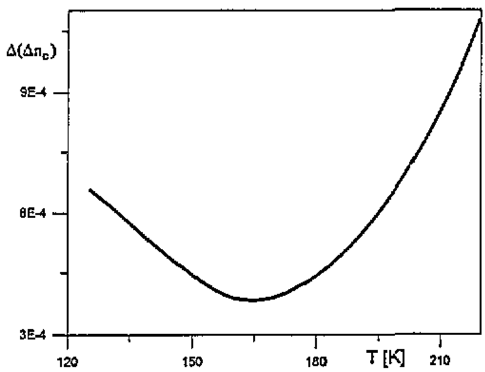

Figure 4. Temperature dependence of the linear birefringence change $\Delta(\Delta n_c)$ for the *c* cut of the MAPCB crystal.

The magnified parts of these dependences revealing anomalies below about 170 K are presented in figure 2. The linear birefringence increments $|\delta(\Delta n_a)|$ and $|\delta(\Delta n_b)|$ below 170 K obtained by subtraction of $|\Delta(\Delta n_a)|$ and $|\Delta(\Delta n_b)|$ from the extrapolated higher-temperature transient (shown in figure 2 as thin lines) are also plotted in figure 2. The temperature derivatives $d(\Delta n_i)/dT$ of the linear birefringence changes are presented in figure 3. These derivatives are very sensitive indications of the linear birefringence anomalies, particularly when the linear birefringence changes are small and diffuse. A very diffuse minimum of $|\Delta(\Delta n_c)|$ at about 165 K is observed (figure 4); so the temperature derivative of $\Delta(\Delta n_c)|$ changes sign (figure 5). The excesses of these derivatives $\delta[d(\Delta n_i)/dT]$ at around 160 K are shown in figure 6. The temperature derivatives of

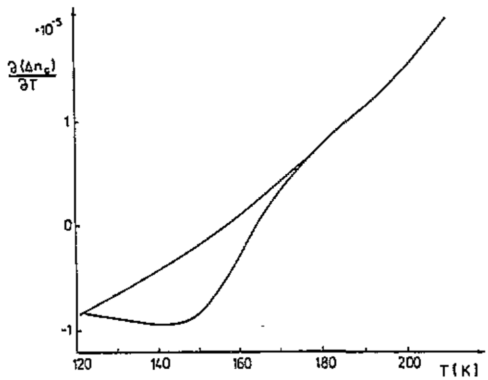

Figure 5. Temperature derivative $d(\Delta n_c)/dT$ of the linear birefringence for the c cut. The thin line represents the extrapolation of the higher-temperature transient of the derivative.

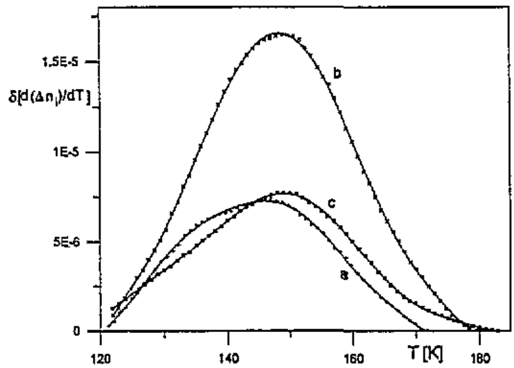

Figure 6. Excesses $\delta[d(\Delta n_i)/dT]$ of the temperature derivatives of the linear birefringence at around 160 K for the a, b and c cuts.

the linear birefringence changes resemble the temperature dependence of the specific heat of the MAPCB crystal [6], and the excesses of these derivatives are very similar to the excess of the specific heat in a similar range of temperatures. The linear birefringence increments induced in the low-temperature region below 170 K can be regarded as the result of an additional contribution from the quadratic electro-optic effect caused by the increment ΔP_S in the polarization observed in a similar temperature range [3, 4]. The linear birefringence increments are then proportional to P_S^2. In figure 7 the plot of ΔP_S^2 versus temperature is given (the ΔP data were taken from [3]). The temperature derivatives of the linear birefringence changes are proportional to the temperature derivative of P_S^2. One can assume, therefore, a linear dependence between the excess entropy and the linear birefringence changes. The specific-heat excess ΔC_p plotted against T and $\Delta c_p/T$ versus T are nearly the same (figure 8) (the ΔC_p date were taken from [6]) taking into account a scaling factor and the temperature range; then the temperature dependence of the specific-heat excess [6] is similar to the temperature dependence of the temperature derivatives of the linear birefringences. Direct comparison of the linear birefringence increments (figure 2) and the ΔP_S^2 and excesses of the temperature derivatives of the linear birefringence and the specific-heat excess is impeded by the distinct relative shift of curves on the temperature scale. The first calorimetric DSC studies [1] reveal a strong anomaly at about 160–170 K, as also do the dielectric constant anomalies reported in [1] and [5] which were started below 180 K.

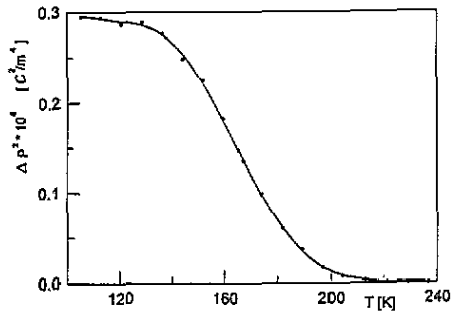

Figure 7. Temperature dependence of ΔP_S^2 (the ΔP_S data were taken from [3]).

The temperature shift may be caused by the various temperature rates used in experiments, by the choice of the background and interpolation to the low-temperature region, by the specific metastability of the transition and by the quality of the crystal. There are also some indications that the polarization has a non-zero component along the b direction in the same temperature range.

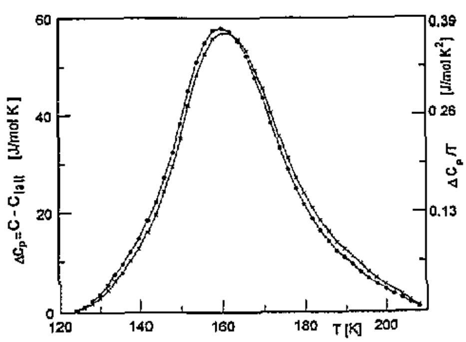

Figure 8. Δc_p (×) and $\Delta c_p/T$ (●) versus T (the Δc_p data were taken from [6]).

Low-temperature anomalies of dielectric, thermal and optical properties can be regarded as possible evidence of the special type of isomorphic ferroelectric–ferroelectric phase transition [8, 9], which is an overcritical transition [6, 9], and for a more quantitative description the free-energy expansion with the eighth-order term in polarization should be used. Following the notation given in [8, 9] one can consider the Landau-type free energy $F = (\alpha/2)p^2 + (\beta/4)p^4 + (\gamma/6)p^6 + (\delta/8)p^8$, where p is the order parameter (polarization), $\alpha = a(T - T_0)$, $a > 0$, and $\beta > 0$, $\gamma > 0$. For $-3/\sqrt{2} < \gamma/\sqrt{\beta\delta} \leqslant -\sqrt{3}$ the isomorphic phase transition takes place. If one assumes that $\beta = \delta = 1$ and taking the scale so that the values $\alpha = 0$ and -0.26 correspond to the temperatures 307 K and 170 K, respectively, one can plot the derivative $|\mathrm{d}(p^2)/\mathrm{d}\alpha|$ (figure 9), which reflects the temperature transients of the linear birefringence derivatives (figure 6). For $\gamma \simeq -1.45$ the calculated curves

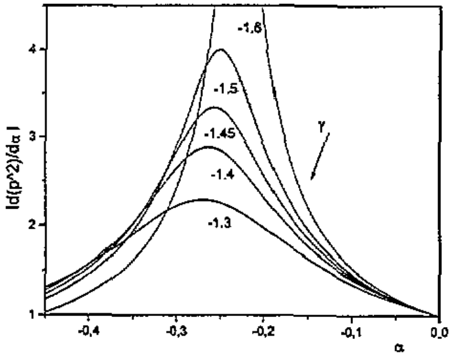

Figure 9. Temperature dependence of $d(p^2)/d\alpha$, for various γ ($\beta = \delta = 1$).

resemble the observed experimental dependences. One can conclude that the temperature dependence of the linear birefringence around 170 K confirms the overcritical character of the thermodynamic behaviour in the MAPCB crystal.

Acknowledgments

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