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The incomplete devil's staircase of betaine calcium chloride dihydrate: acoustic investigation at high pressures

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Abstract. The influence of the hydrostatic pressure on the temperature dependences of the ultrasonic velocities and attenuation coefficients is studied in the vicinity of the phase transition of BCCD crystals. The results obtained are considered within the framework of single- and two-soft-mode models. It is shown that acoustic anomalies are well explained only by the single-soft-mode model, when only one soft mode P_k, which transforms according to the two-dimensional irreducible representation Λ_3 of the $Pnma$ space group, is taken into account.

1. Introduction

Betaine calcium chloride dihydrate $(CH_3)_3NCH_2COO \cdot CaCl_2 \cdot 2H_2O$ (BCCD) shows an especially rich sequence of different commensurate (C) and incommensurate (IC) phases at atmospheric pressure (Rother *et al* 1984, Brill and Ehses 1985, Unruh *et al* 1989). The high-temperature normal (N) phase ($T > T_i = 164$ K) is orthorhombic with the space group $Pnma$ and four molecular units in the unit cell. X-ray measurements, performed by Brill and Ehses (1985), have revealed a one-dimensional modulation with a wavevector $k_i = \delta(T)c^*$ which appears below T_i. The modulation wavevector decreases continuously with decreasing temperature in the IC phases and locks at different rational values of C phases. Unruh *et al* (1989) have identified by dielectric measurements the 15 C-modulated phases with δ equal to (Farrey numbers) $\frac{3}{10}$, $\frac{2}{7}$, $\frac{5}{18}$, $\frac{3}{11}$, $\frac{7}{26}$, $\frac{4}{15}$, $\frac{6}{23}$, $\frac{1}{4}$, $\frac{2}{9}$, $\frac{1}{5}$, $\frac{2}{11}$, $\frac{1}{6}$, $\frac{2}{13}$, $\frac{1}{7}$ and $\frac{1}{8}$. Below $T_F = 46$ K the system undergoes a phase transition (PT) into the proper ferroelectric (F) phase ($\delta = 0/1$) with spontaneous polarization $P_b = 2.4\ \mu\mathrm{K\ cm^{-2}}$. An important relation has been found by Unruh *et al* (1989) between the orientation of the spontaneous polarization in C phases and the ratio m/n. In particular, $P_s \parallel a$ if m is odd and n is even, $P_s \parallel b$ if m is even and n is odd, and $P_s = 0$ when both m and n are odd. This has been considered in detail and explained by Perez-Mato (1988) using group theory methods. However, the precise optical measurements have revealed a small rotation (about 1–2′) of the optical indicatrix starting below T_i and gradually increasing throughout the IC phase (Kroupa *et al* 1990). Obviously, this rotation corresponds to a spontaneous shear strain U_{xz}, which manifests itself as a very small monoclinic distortion of the orthorhombic parent structure. Since one frozen IC wave cannot lower the point-group symmetry, Dvorak (1990) has proposed the two-soft-mode model, according to which two frozen waves of different symmetries but with the same wavevector k occur in the IC phase as well as in all the C phases as a result of the condensation of the two soft modes at $T = T_i$. Two soft modes also have been observed in the Raman and IR spectra (Dvorak 1990, Kamba *et al* 1990). At the same time, many properties of BCCD can be successfully explained using the single-soft-mode model proposed earlier by Perez-Mato (1988). Moreover, the observed rotation of optical indicatrix in the IC phase has not been confirmed by Etxebarria *et al* (1990). They conclude that such a small optical rotation is obviously caused by the possible errors introduced by imperfections in the polarizers.

The incomplete devil's staircase of BCCD has been intensively studied by dielectric (Rother *et al* 1984, Ao *et al* 1989, Unruh *et al* 1989), EPR (Emery *et al* 1990), ultrasonic (Haussuhl *et al* 1988), thermal (Freitag and Unruh 1990) and optical (Etxebarria *et al* 1990, Kroupa *et al* 1990) measurements. Ao *et al* (1989) have studied the pressure–temperature (P–T) phase diagram of BCCD up to 500 MPa and the hypothetical triple Lifshitz point was determined to be at $P_L = 1.25$ GPa and $T_L = 360$ K, where the modulated phase disappears. In this paper we report the original experimental results of the hydrostatic pressure influence on the temperature behaviour of the acoustic properties of BCCD in the pressure region 170–570 MPa and in the temperature range 165–270 K. The results obtained are considered within the framework of phenomenological theory in comparison with single- and two-soft-mode models.

2. Experimental details

Single crystals of BCCD were grown from aqueous solution by the slow evaporation method. The single crystals grown were of a good optical quality. The crystallographic axes were determined by the x-ray diffraction method. We use the standard crystallographic orientation: $a = X = 10.956$ Å, $b = Y = 10.145$ Å and $c = Z = 10.799$ Å. The plane-parallel specimens have typically a 4 mm $\times$ 4 mm $\times$ 4 mm size. All acoustic measurements were performed on the same sample.

The velocity changes of the longitudinal and shear ultrasonic waves (USWs) (f = 10 MHz) were measured by the pulse-echo overlap method (Papadakiz 1967) with an accuracy of 10^{-4}–10^{-5}. The accuracy of the absolute velocity determination was about 0.5%. The thermal expansion correction was not considered for the calculation of the velocity of sound. However, considering the thermal expansion data (Freitag and Unruh 1990) these corrections at atmospheric pressure would affect our results by less than 0.2–0.3%. We assume that the same value of the thermal expansion correction applies to the high-pressure region as well. The ultrasonic attenuation was determined from the decay rate of echo pulses with an accuracy of about 10%. The acoustic waves in the sample were excited by $LiNbO_3$ transducers (resonance frequency $f = 10$ MHz, band width $\Delta f = 0.1$ MHz and acoustic power $P_a = 1$–2 W). Transformer oil was used as a glue between the transducer and the sample. Acoustic investigation under an applied hydrostatic pressure has been performed in cooling runs using a high-pressure camera with a rate of temperature change of about 0.1–0.2 K min^{-1}. Benzene was used as a pressure-transmitting fluid.

3. Experimental results

The temperature dependences of the velocities and attenuation coefficients of the longitudinal and shear USWs at different hydrostatic pressures for BCCD are shown in figures 1–8. The temperature dependences of the longitudinal USW velocity V_l ($q \parallel a$; $E \parallel a$; q is the USW vector and E is the polarization) and attenuation coefficient changes $\Delta\alpha_l$ are shown in figures 1 and 2, respectively. A considerable decrease in V_l and increase in the attenuation coefficient α_l occur at the temperature of the N–IC PT. In the region of the temperature T_F a jump-like decrease in the USW velocity V_l is observed (figure 1, curves labelled 450 MPa and 560 MPa). Insignificant anomalies in the $V_l(T)$ dependences appear also in the region of PTs into the C phases with $\delta = \frac{1}{4}$ and $\delta = \frac{1}{5}$. At the same time the character of the $V_l(T)$ and $\Delta\alpha_l$ dependences are not essentially changed on the whole if the pressure increases. Quite a different situation occurs in the case of the shear USWs. In the low-pressure region the temperature dependence of the shear USW velocity V_6 ($q \parallel a$; $E \parallel b$) (relevant elastic constant C_{66}) shows only a clear kink at T_i (figure 3), while in the high-pressure region a significant decrease in the velocity V_6 and increase in the corresponding attenuation coefficient α_6 (figure 4) occur in the region of the PTs into the C phases with $\delta = \frac{1}{5}$ and $\delta = \frac{1}{7}$, i.e. when m and n are odd. Contrary to this the shear USW velocity V_5 ($q \parallel a$; $E \parallel c$) (figure 5) and attenuation coefficient α_5 (figure 6) show a clear anomalous behaviour in the regions of C phases only with $\delta = \frac{1}{4}$ and $\delta = \frac{1}{6}$, i.e. when m is odd and n is even. In our case the C phases have been identified according to the P–T phase diagram obtained by Ao *et al* (1989). The anomalies in both V_6 and V_5 and in the corresponding attenuation coefficients in the region of the C phases become narrower and sharper with increasing hydrostatic pressure. Finally, the transverse USW velocity V_4 ($q \parallel b$; $E \parallel c$) shows a visible anomalous behaviour in the high-pressure region mainly at the N–IC and IC–F PTs, where a small kink in the $V_4(T)$ dependence and a jump-like increase in V_4 occur at the PT temperatures T_i and T_F, respectively (figure 7). The small kinks in the $V_4(T)$ dependence are also observed at $P = 0.1$ MPa in the vicinity of PTs into the C phase with $\delta = \frac{2}{7}$ (figure 8), which corresponds to the case when m is even and n is odd. The P–T phase diagram obtained from the acoustic investigations (figure 9) is in good agreement with the dielectric measurement data (Ao *et al* 1989, Schaak 1990).

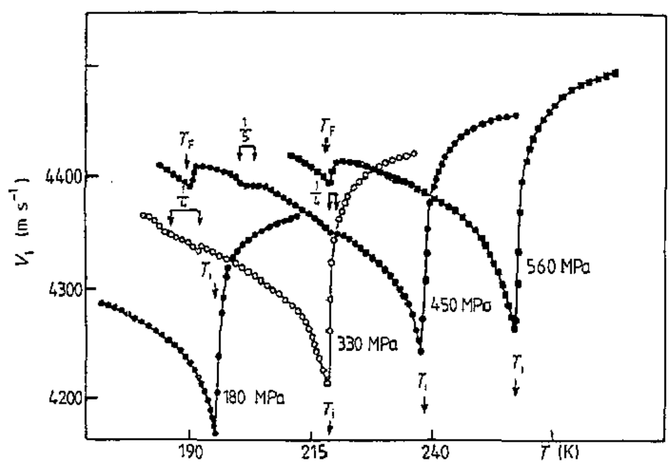

Figure 1. The temperature dependences of the longitudinal USW velocity V_l of BCCD at different pressures P. The regions of the C phase existence in this and subsequent figures are shown by double arrows.

4. Discussion

In the framework of the phenomenological Landau theory the anomalous behaviours of the USW velocity and attenuation in the region of PTs are in general explained on the basis of a

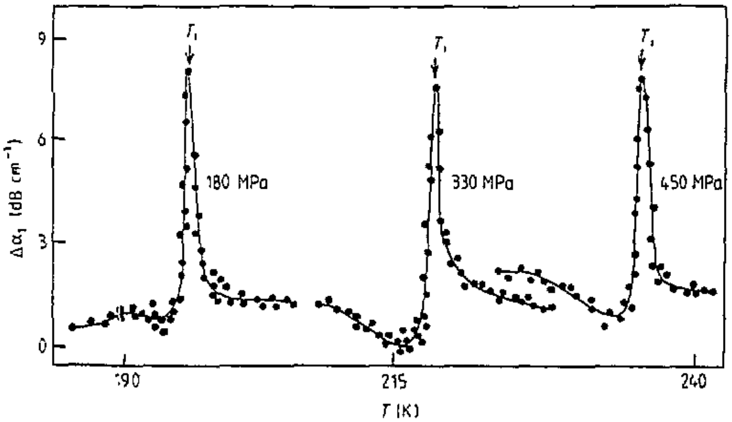

Figure 2. The temperature dependences of the attenuation coefficient changes $\Delta\alpha_1$ for the longitudinal USW velocity V_1 near T_i at different pressures P.

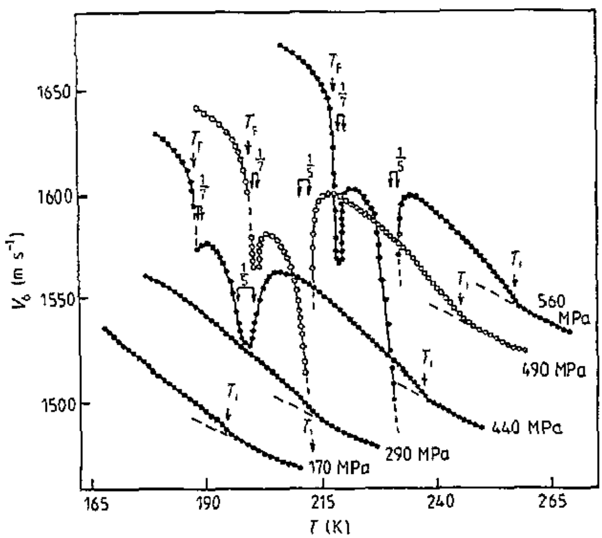

Figure 3. The temperature dependences of the shear USW velocity V_6 of BCCD at different pressures P.

free-energy expansion with the coupling terms, which correspond to anharmonic interaction between the strains U_1–U_6 and the order parameter. It is convenient to use as an order parameter the normal phonon coordinates P_k and Q_k. The space group $Pnma$ contains four two-dimensional irreducible representations at the line Λ ($k = \delta c^*$) of the Brillouin zone. In particular, the matrices of Λ_2 and Λ_3 irreducible representations which are interesting to us are presented in table 1. Here δ takes arbitrary values ($0 < \delta < 1$) including rational values, when $\delta = m/n$ (m and n are integers). In the last case the parity of both m and n defines the possible symmetry of the commensurate modulated phase and n defines the order of the translational invariant with respect to the space group of symmetry in the N phase. Using table 1 it is easy to determine the transformation properties of the nth-order terms, which are constructed from two two-component order parameters (P_k, P_k^*) and (Q_k, Q_k^*). The result of such a consideration is presented in table 2. Only the terms for which the transformation properties are equivalent to the component of the second-rank polar tensor are important with respect to acoustic properties.

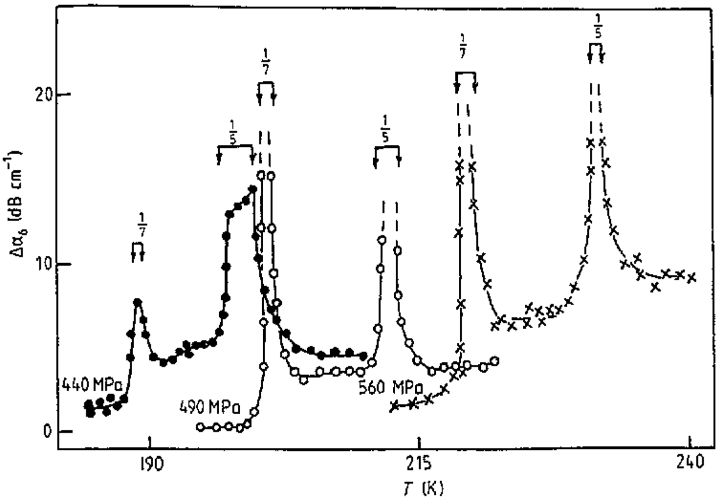

Figure 4. The temperature dependences of the attenuation coefficient changes $\Delta\alpha_6$ for the shear USW velocity V_6 at different pressures P.

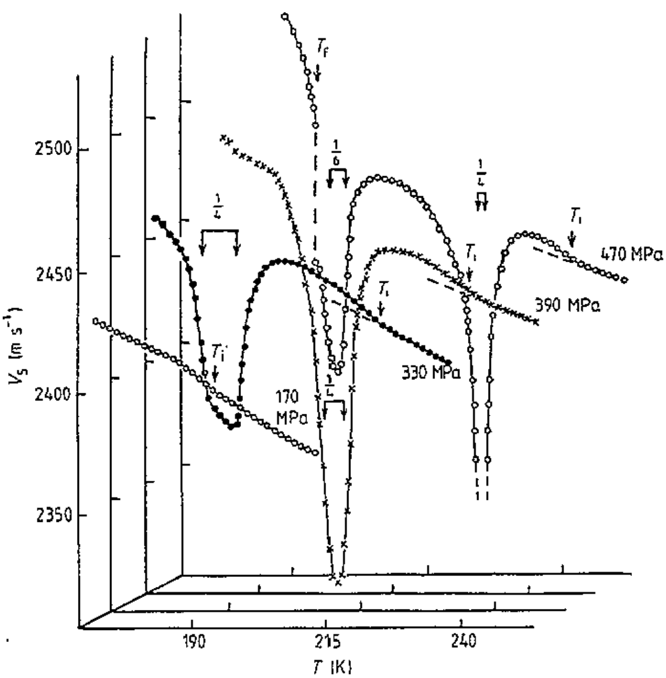

Figure 5. The temperature dependences of the shear USW velocity V_5 of BCCD crystals at different pressures P.

4.1. Single-soft-mode approximation

Firstly, let us consider the real acoustic behaviour in the framework of the single-soft-mode approximation. Only the P_k modes have to be taken into account. Using table 2, the free-energy expansion is written as

$$F_Q = \omega_k^2 P_k P_k^* + \tfrac{1}{2}B(P_k P_k^*)^2 + \tfrac{1}{3}C(P_k P_k^*)^3 + \ldots$$

$$F_{Q,U} = \sum_{i=1}^{3} a_i P_k P_{k-q}^* U_i(q) + \tfrac{1}{2}\sum_{i=1}^{6} b_i P_k P_k^* U_i^2 + \frac{\beta_{m/n}}{n}(P_{m/n}^n + P_{m/n}^{*n})U_i \qquad (1)$$

$$+ \beta_k^*(P_{k_i}^{n-1} P_{mc^*-(n-1)k_i-q} + P_{k_i}^{*n-1} P_{mc^*-(n-1)k_i-q}^*)U_j(q)$$

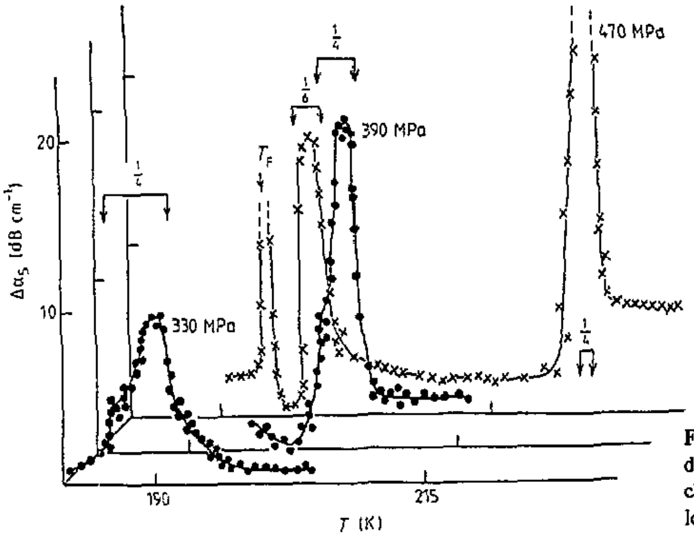

Figure 6. The temperature dependences of the attenuation coefficient changes $\Delta\alpha_5$ for the shear USW velocity V_5 at different pressures P.

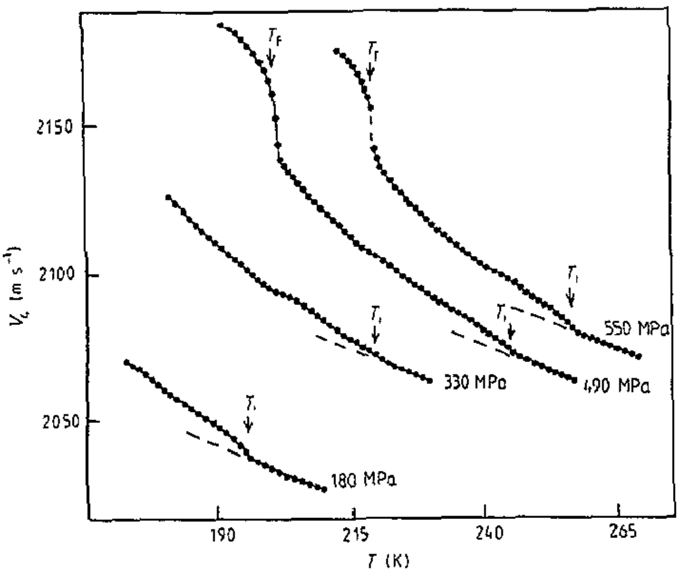

Figure 7. The temperature dependences of the shear USW velocity V_4 of BCCD crystals at different pressures P.

where $\omega_k^2 = A_0(T - T_i) + h(|k_i| - k)^2$ is the soft-mode frequency squared; P_{k_i} and $P_{m/n}$ are the normal mode coordinates in the IC and C phases with $k = (m/n)c^*$, respectively, and $P_{mc^*-(n-1)k_i-q}$ is the change in the $(n-1)$th harmonic modulation normal mode coordinate under the action of USWs. Here $U_j = U_4$ (m is even, and n odd), $U_j = U_5$ (m is odd, and n even) and $U_j = U_6$ (m is odd, and n odd). If we take into account the splitting of the soft mode in the IC phase on the amplitudon and phason branches (Dvorak and Petzelt 1978), it is possible to express the changes in the complex elastic modulus in the IC and C phases as

$$\Delta C_{ii}^* = b_i P_*^2 - 2a_i^2 P_*^2/\omega_A^2(q)[1 + i\Omega\tau_A(q)] \qquad \text{(IC phase)} \qquad i = 1\text{–}3 \tag{2}$$

$$\Delta C_{ii}^* = b_i P_{m/n}^2 - 2a_i^2 P_{m/n}^2/\omega_{m/n}^2(q)[1 + i\Omega\tau_{m/n}(q)] \qquad \text{(C phase)} \qquad i = 1\text{–}3 \tag{3}$$

$$\Delta C_{ii}^* = b_i P_*^2 - \tfrac{1}{2}\beta_k^2 P_*^{2n-2}\{1/\omega_A^2(K)[1 + i\Omega\tau_A(K)] + 1/\omega_{\varphi_{mn}}^2(K)[1 + i\Omega\tau_{\varphi_{mn}}(K)]\}$$
$$\text{(IC phase)} \qquad i = 4\text{–}6 \tag{4a}$$

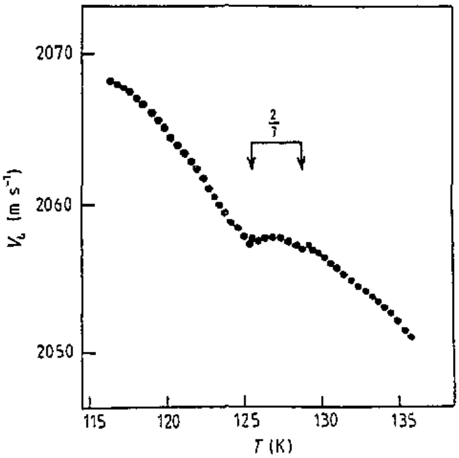

Figure 8. The temperature dependences of the transverse USW velocity V_4 in the region of existence of the C phase with $\delta = \frac{2}{7}$ at $P = 0.1$ MPa.

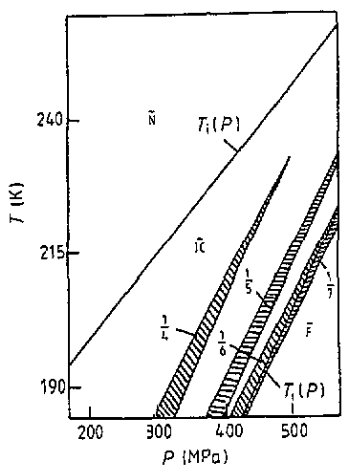

Figure 9. P–T phase diagram of BCCD crystals. The shaded regions in the P–T plane correspond to C phases with different values of modulation parameter $\delta = m/n$.

Table 1. Matrices of the irreducible representations Λ_2 and Λ_3 at the line $\Lambda(k = \delta c^*)$ for the space group $Pnma$. The origin is on the inversion centre. $\epsilon^* = \exp(i\pi\delta)$; $\epsilon = \exp(-i\pi\delta)$.

Base	$E\|000$	$C_{2x}\|\frac{1}{2}\frac{1}{2}\frac{1}{2}$	$C_{2y}\|0\frac{1}{2}0$	$C_{2z}\|\frac{1}{2}0\frac{1}{2}$	$I\|000$	$\sigma_x\|\frac{1}{2}\frac{1}{2}\frac{1}{2}$	$\sigma_y\|0\frac{1}{2}0$	$\sigma_z\|\frac{1}{2}0\frac{1}{2}$	
Q_k Q_k^*	$\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}$	$\begin{pmatrix}0 & -\epsilon^*\\-\epsilon & 0\end{pmatrix}$	$\begin{pmatrix}0 & -1\\-1 & 0\end{pmatrix}$	$\begin{pmatrix}\epsilon^* & 0\\0 & \epsilon\end{pmatrix}$	$\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}$	$\begin{pmatrix}-\epsilon^* & 0\\0 & -\epsilon\end{pmatrix}$	$\begin{pmatrix}-1 & 0\\0 & -1\end{pmatrix}$	$\begin{pmatrix}0 & \epsilon^*\\\epsilon & 0\end{pmatrix}$	Λ_2
P_k P_k^*	$\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}$	$\begin{pmatrix}0 & \epsilon^*\\\epsilon & 0\end{pmatrix}$	$\begin{pmatrix}0 & -1\\-1 & 0\end{pmatrix}$	$\begin{pmatrix}-\epsilon^* & 0\\0 & -\epsilon\end{pmatrix}$	$\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}$	$\begin{pmatrix}\epsilon^* & 0\\0 & \epsilon\end{pmatrix}$	$\begin{pmatrix}-1 & 0\\0 & -1\end{pmatrix}$	$\begin{pmatrix}0 & -\epsilon^*\\-\epsilon & 0\end{pmatrix}$	Λ_3

$$\Delta C_{ii}^* = b_i P_{m/n}^2 - \beta_{m/n}^2 P_{m/n}^{2n-2} / 2\omega_{m/n}^2(q)[1 + i\Omega\tau_{m/n}(q)] \qquad (\text{C phase}) \qquad i = 4\text{–}6 \quad (4b)$$

where $\Omega = qV$ is the USW frequency, $\omega_A^2(q) = 2A_0(T_i - T) + hq^2$ and $\tau_A(q)$ are the amplitudon frequency and relaxation time, respectively, $\omega_{\varphi_{mn}}^2(K) = hK^2 = h[(n\delta - m)c^*]^2$ and $\tau_{\varphi_{mn}}(K)$ are the phason frequency and relaxation time, P_* is the equilibrium value of the order parameter amplitude in the IC phase, and $\omega_{m/n}^2(q)$ and $\tau_{m/n}(q)$ are the soft mode frequency and relaxation time in the C phase. Using the well known relation between changes ΔC_{ii}^* in the complex elastic modulus, changes ΔV_i in the ultrasonic velocities and

Table 2. Transformation properties of the nth-order terms constructed from two two-component order parameters $(Q_k, Q_k^*) \in \Lambda_2$ and $(P_k, P_k^*) \in \Lambda_3$ at the Λ line ($k = \delta c^*$) for the space group $Pnma$. Even and odd parities of m, n, r, s are indicated by the signs + and −, respectively. The integers r and s satisfy the condition $r + s = n$.

m, n	Term	Transformation properties
m and n are arbitrary	$P_k Q_k^* + P_k^* Q_k$	XZ
	$P_k Q_k^* - P_k^* Q_k$	X
	$P_k^2 Q_k^{*2} - P_k^{*2} Q_k^2$	Z
	$P_k P_k^*$; $Q_k Q_k^*$	X^2, Y^2, Z^2
$m(-), n(+)$	$P_k^{r-} Q_k^{s-} + P_k^{*r-} Q_k^{*s-}$	X^2, Y^2, Z^2
	$P_k^{r-} Q_k^{s-} - P_k^{*r-} Q_k^{*s-}$	Z
	$P_k^{r+} Q_k^{s+} + P_k^{*r+} Q_k^{*s+}$	XZ
	$P_k^{r+} Q_k^{s+} - P_k^{*r+} Q_k^{*s+}$	X
	$P_k^n + P_k^{*n}$	XZ
	$P_k^n - P_k^{*n}$	X
	$Q_k^n + Q_k^{*n}$	XZ
	$Q_k^n - Q_k^{*n}$	X
$m(+), n(-)$	$P_k^{s-} Q_k^{r+} + P_k^{*s-} Q_k^{*r+}$	YZ
	$P_k^{s-} Q_k^{r+} - P_k^{*s-} Q_k^{*r+}$	Y
	$P_k^{s+} Q_k^{r-} + P_k^{*s+} Q_k^{*r-}$	XY
	$P_k^{s+} Q_k^{r-} - P_k^{*s+} Q_k^{*r-}$	XYZ
	$P_k^n + P_k^{*n}$	YZ
	$P_k^n - P_k^{*n}$	Y
	$Q_k^n + Q_k^{*n}$	XY
	$Q_k^n - Q_k^{*n}$	XYZ
$m(-), n(-)$	$P_k^{s-} Q_k^{r+} + P_k^{*s-} Q_k^{*r+}$	XY
	$P_k^{s-} Q_k^{r+} - P_k^{*s-} Q_k^{*r-}$	XYZ
	$P_k^{s+} Q_k^{r-} + P_k^{*s+} Q_k^{*r-}$	YZ
	$P_k^{s+} Q_k^{r-} - P_k^{*s+} Q_k^{*r-}$	Y
	$P_k^n + P_k^{*n}$	XY
	$P_k^n - P_k^{*n}$	XYZ
	$Q_k^n + Q_k^{*n}$	YZ
	$Q_k^n - Q_k^{*n}$	Y

changes $\Delta\alpha_i$ in the attenuations given by

$$\Delta V_i/V_i = \mathrm{Re}(\Delta C_{ii}^*)/2C_{ii} \qquad \Delta\alpha_i = \Omega\,\mathrm{Im}(\Delta C_{ii}^*)/2C_{ii} \tag{5}$$

and combining in pairs equations (2) and (3), and equations (4a) and (4b), for changes ΔV_i in the longitudinal and shear USW velocities and changes $\Delta\alpha_i$ in the attenuation in the PT regions we obtain

$$\Delta V_i = (1/2\rho V_i)[b_i P_*^2 - 2a_i^2 P_*^2/\omega_A^2(1+\Omega^2\tau_A^2) + b_i P_{m/n}^2 - 2a_i^2 P_{m/n}^2/2\omega_{m/n}^2(1+\Omega^2\tau_{m/n}^2)] \qquad i = 1\text{–}3 \tag{6a}$$

$$\Delta\alpha_i = (1/\rho V_i^2)[2a_i^2 P_*^2 \Omega^2 \tau_A/\omega_A^2(1+\Omega^2\tau_A^2) + 2a_i^2 P_{m/n}^2 \Omega^2 \tau_{m/n}/\omega_{m/n}^2(1+\Omega^2\tau_{m/n}^2)] \qquad i = 1\text{–}3 \tag{6b}$$

$$\Delta V_i = (1/2\rho V_i)[b_i P_*^2 - \beta_k^{*2} P_*^{2n-2}/2\omega_{\varphi_m}^2(1+\Omega^2\tau_{\varphi_{mn}}^2) + b_i P_{m/n}^2 - \beta_{m/n}^2 P_{m/n}^{2n-2}/2\omega_{m/n}^2(1+\Omega^2\tau_{m/n}^2)] \qquad i = 4\text{–}6 \tag{7a}$$

$$\Delta\alpha_i = (1/\rho V_i^2)[\beta_k^{*2} P_*^{2n-2}\Omega^2\tau_{\varphi_{mn}}/2\omega_{\varphi_{mn}}^2(1+\Omega^2\tau_{\varphi_{mn}}^2) + \beta_{m/n}^2 P_{m/n}^{2n-2}\Omega^2\tau_{m/n}/2\omega_{m/n}^2(1+\Omega^2\tau_{m/n}^2)] \qquad i = 4\text{–}6. \tag{7b}$$

As usual, in equations (7), only the phason contribution is considered since, far from the temperature T_i, $\omega_A \gg \omega_\varphi$. We assume that $P_{m/n} \neq 0$ only at $\delta = m/n$, while $P_* \neq 0$ only when $\delta \neq m/n$. In the opposite case, when the IC and C phases coexist in some temperature region in the vicinty of IC–C PTs, the corresponding contribution should be multiplied by the volume ratio function of the corresponding C or IC phase in the sample. The details of this procedure have been described by Folcia and Perez-Mato (1990) relative to the dielectric permittivity behaviour in a similar IC system $(N(CH_3)_4)_2XCl_4$ ($X \equiv$ Co, Zn).

As follows from equation (6*a*), the velocity V_1 should exhibit a sharp decrease at $T = T_i$, caused by the interaction between the USW and amplitudon, while the anomalous attenuation increases according to equation (6*b*). Such a case was observed experimentally (figures 1 and 2). The visible continuous decrease in the USW velocity V_1 above T_i is caused by fluctuation of the order parameter. The fluctuation effects in IC systems concerning the acoustic properties have been considered in detail by Li *et al* (1990). The smooth changes in the USW velocity V_1 in the region of PTs into C phases with $\delta = \frac{1}{4}$ and $\delta = \frac{1}{5}$ (curves labelled 330 MPa and 450 MPa in figure 1) may also be explained if we take into account the third and fourth terms in equation (6*a*). The temperature changes in the shear USW velocities V_4–V_6 near the N–IC PT are mainly caused by the first terms in equation (7*a*), which leads to the quadratic dependence of ΔV_i on the order parameter amplitude in the IC phase. Consequently, the kinks in $V_i(T)$ are observed at $T = T_i$ (figures 3, 5 and 7). The strong decrease in the USW velocities V_5 and V_6 and the increase in the corresponding attenuation coefficients α_5 and α_6 in the IC phase near the PTs to the C phases with $\delta = \frac{1}{4}$ and $\frac{1}{6}$ and $\delta = \frac{1}{5}$ and $\frac{1}{7}$, respectively, is caused by the phason contribution. This is due to the faster increase in $P_*^{2n-2}/\omega_{\varphi_{mn}}^2$ (at $\delta \to m/n$, $\omega_{\varphi_{mn}} \to 0$) comparatively with P_*^2. In the C phases, acoustic softening may be easily explained by the last terms in equations (7). As follows from experimental data, the acoustic anomalies near the corresponding C phases are enhanced at high pressures. This shows that the values of the jumps in the $\delta(T)$ dependence at the first-order PTs into these C phases decrease gradually with increasing hydrostatic pressure. Unfortunately, numerical calculation of these contributions to the acoustic properties has not been carried out since experimental data concerning the $\delta(T, P)$ dependence are not available. However, in any case, as follows from group theory considerations, acoustic softening should be observed for V_5 in the vicinity of C phases with $\delta = \frac{1}{4}$ and $\frac{1}{6}$, for V_6 in the vicinity of C phases with $\delta = \frac{1}{5}$ and $\frac{1}{7}$ and, finally, for V_4 when $\delta = \frac{2}{7}$ and $\frac{2}{9}$. These predictions are in good agreement with the experimental data (figures 3–8) which suggests the validity of the single-soft-mode approximation used to explain the acoustic properties on the devil's staircase of BCCD.

4.2. Acoustic properties in the framework of the two-soft-mode model

According to the two-soft-mode model, proposed by Dvorak (1990), the two soft modes P_k and Q_k, which transform according to the two-dimensional irreducible representations Λ_3 and Λ_2, respectively, of the *Pnma* space group symmetry, both condense simultaneously at nearly the same temperature in the vicinity of T_i. Firstly, let us consider the mixed terms containing simultaneously both components P_k and Q_k (table 2). The lowest-order mixed invariant is $U_5(P_k Q_k^* + P_k^* Q_k)$. In the framework of the phenomenological Landau theory such a term causes a step-like decrease in the sound velocity V_5 and an increase in the attenuation coefficient α_5 at $T = T_i$. However, only kinks in the $V_5(T)$ dependences are really observed near T_i (figure 5), while the anomalous attenuation for this USW is quite absent. Mixed-coupling terms $U_6(P_k^{s+}Q_k^{r-} + P_k^{*s+}Q_k^{*r-})$ and $U_4(P_k^{s+}Q_k^{r-} + P_k^{*s+}Q_k^{*r-})$ are also not evident in the region of C phases with $\delta = m(+)/n(-)$ and $\delta = m(-)/n(-)$, respectively, in the corresponding temperature dependences of the USW velocities and attenuation coefficients (figures 3, 4 and 7). Moreover, even the pure-coupling invariants $U_6(Q_k^n + Q_k^{*n})$ and $U_4(Q_k^n + Q_k^{*n})$ do not evoke anomalous behaviour of the USW velocities V_6 and V_4 in the vicinity of these C phases. All these facts clearly show that the frozen Q_k mode induces probably a very weak distortion and consequently is almost not evident in the acoustic properties.

5. Conclusion

We have investigated the hydrostatic pressure influence on the temperature dependences of the longitudinal and shear USW velocities and attenuation coefficients of BCCD. Clear decreases in sound velocities and increases in the corresponding attenuation coefficients were observed: for shear USWs, V_4 ($q \parallel b$; $E \parallel c$) in the vicinity of the C phase with the modulation parameter $\delta = \frac{2}{7}$, V_5 ($q \parallel a$; $E \parallel c$) in the region of C phases with $\delta = \frac{1}{4}$ and $\frac{1}{6}$ and V_6 ($q \parallel a$; $E \parallel b$) in the vicinity of C phases with $\delta = \frac{1}{5}$ and $\frac{1}{7}$. This has been considered in detail in the framework of the single-soft-mode model (Perez-Mato 1988) and two-soft-mode model (Dvorak 1990) using the group theory method. Such an analysis shows that acoustic anomalies are in good agreement with the single-soft-mode model, when only one soft mode P_k, transforming according to the two-dimensional irreducible representation Λ_3 of the *Pnma* space group symmetry, is taken into account.

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