Unusual low-frequency elastic anomalies around the upper incommensurate phase of $[NH_3C_3H_7]_2MnCl_4$

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Low-frequency elastic properties (1–15 Hz) of $[NH_3C_3H_7]_2MnCl_4$ crystals have been investigated in the phase transition region to the upper incommensurate phase (γ phase). We have found that the character of the elastic anomalies is essentially different near T_i and T_c although the symmetry breaking at these phase transitions is equivalent. In addition the anomalies both in real and imaginary part of complex effective elastic constants are strongly frequency dependent in the range of 1–15 Hz. This unusual elastic behavior in the region of the reentrant β-γ-δ phase sequence is treated within the framework of a phenomenological theory.

I. INTRODUCTION

Bis-propylammonium tetrachloromanganate (PAMC) $[NH_3C_3H_7]_2MnCl_4$ is a unique compound among structurally incommensurate dielectric crystals due to its complicated phase sequence with two unusual incommensurate phases.[1–3] On cooling, PAMC shows the following sequence of phases:

$$\alpha(D_{4h}^{17}) \xrightarrow[440\ \mathrm{K}]{T_0} \beta(D_{2h}^{18}) \xrightarrow[393\ \mathrm{K}]{T_i} \gamma(\mathrm{inc}) \xrightarrow[343\ \mathrm{K}]{T_c} \delta(D_{2h}^{18}) \xrightarrow[163\ \mathrm{K}]{T_i'} \epsilon(\mathrm{inc}) \xrightarrow[114\ \mathrm{K}]{T_c'} \xi(C_{2h}^{5})$$

where γ and ϵ are the incommensurate phases. Especially extraordinary is the upper incommensurate phase γ, since it is sandwiched between two phases β and δ which have the same symmetry, i.e., the normal phase is reentrant. Structurally, PAMC is a representative of the perovskite-type layer structures with formula $(C_nH_{2n+1}NH_3)_2MCl_4$ ($n<5$). The layers of corner-sharing $MnCl_6$ octahedra forming sheets of perovskite are sandwiched between layers of $C_3H_7NH_3$ propylammonium chains. Dynamically disordered rigid propylammonium chains are hydrogen bonded to the $MnCl_6$ octahedra. The resulting neutral strata stack on each other and are held together by van der Waals interactions.[4] The phase transition into incommensurate phase γ is associated with the condensation of the soft mode at the wave vector

$$q_\gamma = (1/6+\delta)c^* + b^* \quad (1)$$

belonging to the H line (between the Y and T point) of the orthorombic base centered Brillouin zone.[2] The incommensurate structure is characterized by a modulation of the interlayer distance with an amplitude in the y direction (perpendicular to layers) and a wave vector in the z direction (parallel to layers). In contrast to the usual lock-in transition in the improper incommensurate ferroelectric and ferroelastic crystals, where the amplitude of the modulation wave continues to increase at T_c and the modulation parameter δ gradually vanishes, in PAMC the amplitude of the incommensurate modulation wave vanishes on both sides of the γ phase, whereas the wave-vector behavior is not critical. The structure determination of the incommensurate γ phase shows that the modulation wavelength is about 40 Å and the amplitude ~0.5 Å. The value of modulation wavelength is practically unchanged in the whole temperature range of the γ phase.

From the point of view of the phenomenological Landau theory the β-γ-δ phase sequence is very interesting and ruther unusual. The treatment frequently used for the usual improper incommensurate ferroelectrics or ferroelastics with a thermodynamical potential where the order parameter is expanded around the commensurate wave vector k_c, cannot be applied in the case of the γ phase in PAMC. A hypothetical direct transition from β to δ phase would be connected with a non-symmetry-breaking order parameter. The unusual temperature behavior of the incommensurate modulation amplitude according to Kind and Muralt[5] appears as a result of a strong coupling between the inhomogeneous order parameter η and this totally symmetric order parameter e. The specific feature of the PAMC compound is an unusually high thermal expansion perpendicular to the layers.[6] Since this thermal expansion is associated with the spontaneous strain component $e_{yy}=e_2$, which transforms according to the identity representation of the β phase, it was identified with the non-symmetry-breaking order parameter.[5] A renormalization of some initial expansion coefficients due to the higher-order coupling terms between η and e_2 is the essential reason for the reentrant behavior of the γ phase.

Thus PAMC is an extraordinary system where the anharmonic effects are strongly developed. It is obvious that this big anharmonicity should manifest itself also in the elastic

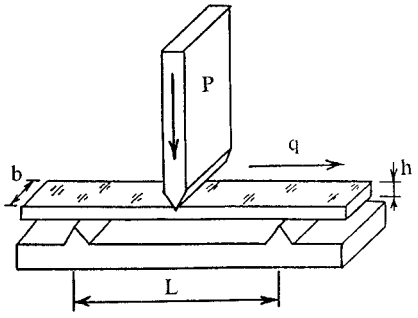

FIG. 1. Three-point-bending geometry.

properties. Therefore the performance of corresponding measurements is timely without doubt. In the present paper we report the original experimental results on low-frequency (1–15 Hz) elastic investigations of the phase transitions into the upper incommensurate γ phase. The obtained results are discussed within the framework of a phenomenological Landau theory.

II. EXPERIMENTAL RESULTS

Single crystals PAMC were grown by slow evaporation of an aqueous solution of equimolar amounts of $2NH_3C_3H_7Cl$ and $MnCl_2 \cdot 4H_2O$. The crystals were oriented under a polarizing microscope, and samples for measurements were cleaved parallel to the layers. We used the crystallographic orientation where the perovskite layers are perpendicular to the z axis. This setting differs from that used in other references (e.g., from Kind and Muralt[5]).

The low-frequency elastic measurements were performed by the three-point-bending method using a dynamical mechanical analyser (Perkin-Elmer DMA-7). The sample geometry for this method is presented in Fig. 1. The relation between the effective spring constant K measured by DMA-7 and Young's modulus is determined by the following equation:[7]

$$K = Y(\mathbf{q}) 4b(h/L)^3 [1 + 1.5(h/L)^2 Y(\mathbf{q})/G(\mathbf{pq})]^{-1}, \quad (2)$$

where the geometrical parameters b, h, and L of the sample are shown in Fig. 1, $Y(\mathbf{q})$ is the Young's modulus along the $\mathbf{q}$ direction, and $G(\mathbf{pq})$ is the shear modulus. Since the values of $Y(\mathbf{q})$ and $G(\mathbf{pq})$ are of the same order and the ratio $(h/L)^2$ in our measurements is ~ 0.01 we will neglect the second contribution in Eq. (2). In this case the Young's modulus $Y(\mathbf{q})$ is simply proportional to the effective spring constant K. In the dynamic mode of the DMA-7 a sinusoidal force $P(T) = P_0 e^{i\omega t}$ is applied to the sample resulting in a sinusoidal change in length of the sample. If the specimen has an internal friction, there is a phase shift between the applied stress and the resulting deformation $U(t) = U_0 e^{i(\omega t - \delta)}$ measured by the sensitive electromechanical system of DMA-7. In this case the spring constant and the Young's modulus are complex:

$$K^* = P(t)/U(t) = K' + iK'', \quad (2a)$$

$$Y^*(q) = Y'(q) + iY''(q), \quad (2b)$$

where $K' = (P_0/U_0)\cos\delta$, $K'' = (P_0/U_0)\sin\delta = K' tg\,\delta$, $Y'(q) \sim K'$, and $Y''(q) \sim K''$. Since the absolute accuracy of the low-frequency elastic measurements is usually not better than 20% the corresponding results will be presented in a relative form for the real $[C_r'(\mathbf{q}) = Y'(\mathbf{q})/Y_0'(\mathbf{q})]$ and imaginary $[C_r''(\mathbf{q}) = C_r'(\mathbf{q}) tg\,\delta]$ parts of the effective complex elastic constant $C_r^*(\mathbf{q})$, where the value for $Y_0'(\mathbf{q})$ is taken at 400 K. The accuracy in this case was about 1%. Elastic measurements have been performed at heating with a rate of temperature change of about 0.5 K/min.

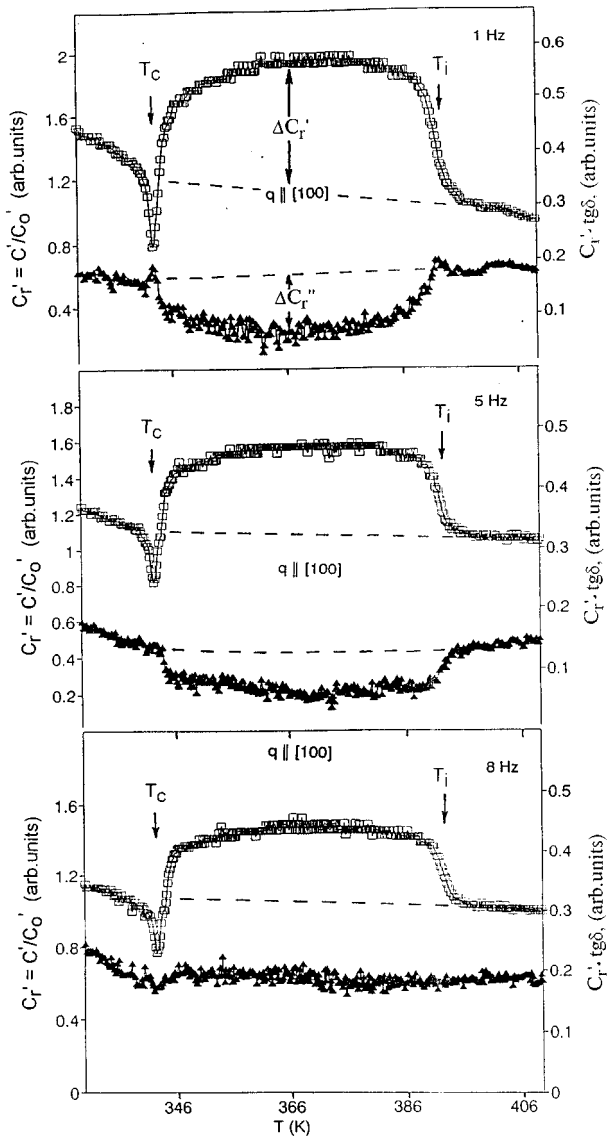

FIG. 2. Measured temperature dependences of the relative real $C_r' = C'/C_0'$ (□) and imaginary $C_r'' = C_r' tg\,\delta$ (▲) parts of the complex effective elastic constant $C_r^*[100]$ for different frequencies. C_0' corresponds to $T = 400$ K.

The temperature dependences of the real and imaginary parts of the effective complex elastic constants $C_r^*(\mathbf{q} \| [100])$ and $C_r^*(\mathbf{q} \| [110])$ at different frequencies (1, 5, and 8 Hz) are presented in Fig. 2 and Fig. 3, respectively. The changes of the effective elastic constants C_r^* are associated with the temperature behavior of Young's moduli $Y([100])$ and $Y([110])$, which can be expressed through the elastic compliences as follows:

$$Y^{-1}[100] = S_{11}/2 + S_{22}/2, \quad (3a)$$

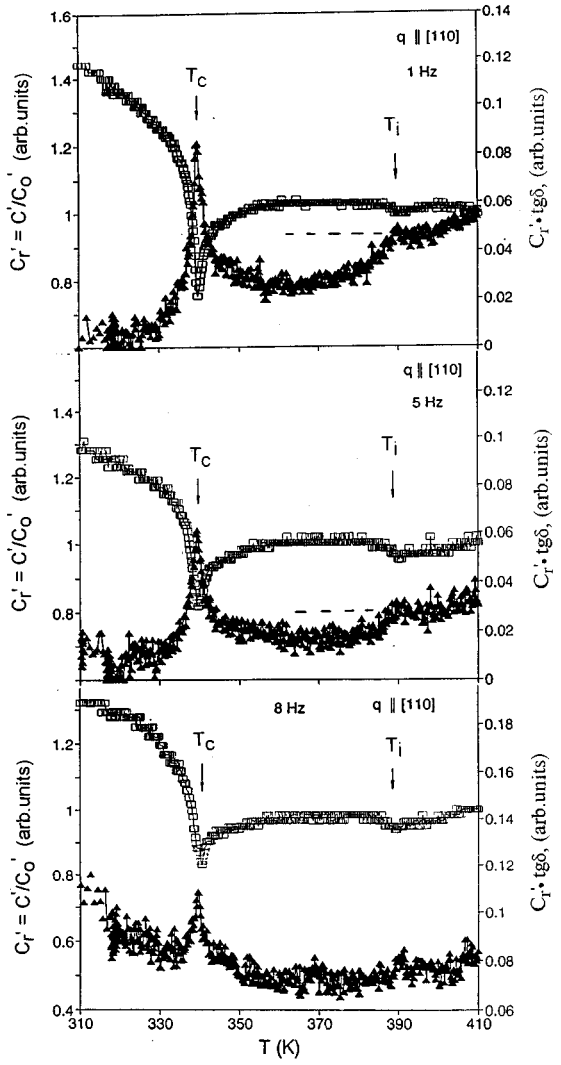

FIG. 3. Measured temperature dependences of the relative real $C_r'=C'/C_0'$ (□) and imaginary $C_r''=C_r' tg\,\delta$ (▲) parts of the complex effective elastic constant $C_r^*[110]$ for different frequencies. C_0' corresponds to $T=400$ K.

$$Y^{-1}[110]=(S_{11}+S_{22}+S_{66}+2S_{12})/4, \tag{3b}$$

where the second contribution in Eq. (3a) is introduced due to the existence of a polidomain structure with 90° domains. In the geometry $\mathbf{q}\|[110]$ the polidomain structure does not influence the effective magnitude of $Y^{-1}[110]$. The domains immediately appear below $T_0=440$ K and exist in the β, γ, and δ phases. As follows from Figs. 2 and 3, both geometries of elastic measurements show clear anomalous behavior in the region of the phase transitions (at T_i and T_c) into the incommensurate γ phase. In connection with this we would like to point out that several facts are rather unusual at a first glance.

(i) The character of the elastic anomalies is essentially different near T_i and T_c although the symmetry breaking at these phase transition points is equivalent.

(ii) The magnitudes of the elastic anomalies near T_c in the real parts of both complex effective elastic constants $C_r^*([100])$ and $C_r^*([110])$ and in the imaginary part of $C_r^*([110])$ decrease essentially with increasing frequency.

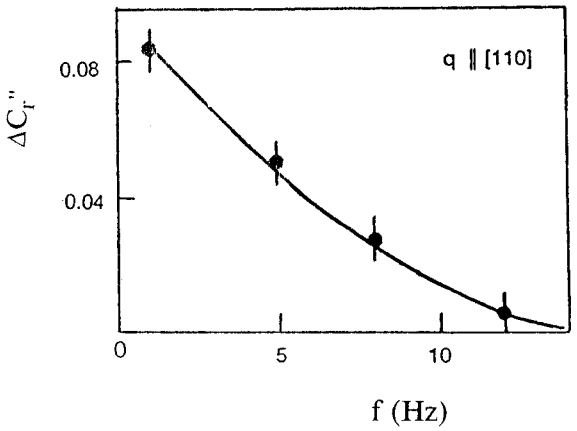

FIG. 4. Frequency dependences of the anomalous contributions into the imaginary part $\Delta C_r''$ (see Fig. 3) of the complex effective elastic constant $C_r^*[110]$ at $T=T_c$.

Particularly, the anomalous peak in the temperature behavior of $C_r''([110])$ cannot be observed near T_c at frequencies higher than 12 Hz (see Fig. 4).

(iii) The phase transition from the β to the γ phase at T_i is accompanied by a clear decrease in the imaginary parts of both complex elastic constants $C_r^*([100])$ and $C_r^*([110])$, while the real part of $C_r^*([100])$ essentially increases. In addition the corresponding spontaneous contributions $\Delta C_r' = C_r'(T)-C_r'(\text{extr})$ and $\Delta C_r''=C_r''(T)-C_r''(\text{extr})$ [where $C_r'(\text{extr})$ and $C_r''(\text{extr})$ are the extrapolations of the $C_r'(T)$ and $C_r''(T)$ dependences from the high-temperature phase (see Fig. 2)] are also strongly frequency dependent (Fig. 5).

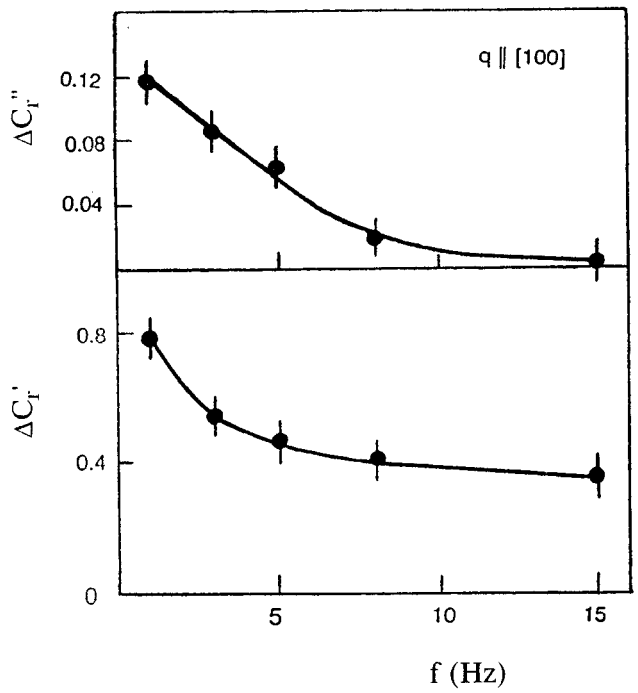

FIG. 5. Frequency dependences of the anomalous contributions into the real ($\Delta C_r'$) and imaginary ($\Delta C_r''$) parts (see Fig. 2) of the complex effective elastic constant $C_r^*[100]$ at $T=366$ K.

III. LANDAU THEORY APPROACH

Let us consider the obtained results in the framework of a phenomenological theory. The elastic compliences S_{11}, S_{22}, S_{66}, and S_{12} [see Eqs. 3(a) and 3(b)] are expressed through the elastic constants C_{ij} by the following equations:

$$S_{11}=(C_{22}C_{33}-C_{23}^2)/\Delta, \tag{4a}$$

$$S_{22}=(C_{11}C_{33}-C_{13}^2)/\Delta, \tag{4b}$$

$$S_{12}=(C_{23}C_{13}-C_{12}C_{33})/\Delta, \tag{4c}$$

$$S_{66}=1/C_{66}, \tag{4d}$$

$$\Delta=C_{11}C_{22}C_{33}+2C_{12}C_{13}C_{23}-C_{22}C_{13}^2-C_{11}C_{23}^2-C_{33}C_{12}^2.$$

The complicated combinations of many elastic constants, which according to Eqs. (4a)–(4d) give the contributions to the resulting elastic compliences S_{ij}, create a problem for a quantitative analysis. Therefore we will perform only a qualitative description considering the anomalous behavior of separate elastic constants C_{ij}. The strong anharmonicity, which manifests itself in the behavior of the elastic properties in the region between the phase transitions into the incommensurate γ phase can be explained in two ways. The first one is based on the model of anharmonic interactions between the order parameter of the γ phase η_q and the order parameter r. The last one appears below T_0 due to the upper phase transition ($D_{4h}^{17}\rightarrow D_{2h}^{18}$) and exists in all low-temperature phases including the β, γ, and δ phase. The second model considers the anharmonic interactions between the order parameter of the γ phase η_q and the non-symmetry-breaking order parameter e_2. We are presenting here only the first considerations, since the two models are equivalent in the sense that the non-symmetry-breaking order parameter e_2 appears as a result of the upper phase transition, i.e., the order parameter e_2 can be considered as a secondary order parameter with respect to the primary order parameter r ($e_2\sim r^2$). One can note that the reentrant behavior of the γ phase can be successfully explained in a quite similar way to Ref. 5 if instead of the coupling between η_q and e_2 we will consider the interaction between η_q and r leading to the renormalization of some initial coefficients in the free energy expansion. For example the coupling $\eta_q\eta_q^*r^2$ (in our case) is equivalent to the coupling $\eta_q\eta_q^*e_2$ (in the case of Kind and Muralt[5]) since $e_2\sim r^2$.

The group theoretical consideration of the phase transition $D_{4h}^{17}\rightarrow D_{2h}^{18}$ has been performed by Petzelt[8] for the isomorphous layered compound $(CH_3NH_3)_2MnCl_4$. It is connected with the condensation of the soft mode at the X point of the Brillouin zone of the D_{4h}^{17} structure. The star of the irreducible representation consists of two k vectors, therefore the corresponding irreducible representations of the space group D_{4h}^{17} are two-dimensional and the order parameter has two components r_1 and r_2. However, the case when both r_1 and r_2 are nonzero in the distorted phase, leads to an eightfold unit cell which is not observed in the investigated compound. The phase transition $D_{4h}^{17}(z=1)\rightarrow D_{2h}^{18}(z=2)$ corresponds to the more simple case $r_1=r$ and $r_2=0$ or $r_1=0$ and $r_2=r$, which are physically equivalent and leads to two types of 90° domains observed below T_0. The soft mode transforms according to the τ_5 representation at the X point. Knowing the transformation properties of both order parameters r and η_q the free-energy expansion can be written as follows:

$$F=F_\eta+F_r+F_{r\eta u}, \tag{5}$$

$$F_\eta=\tfrac{1}{2}A_q\eta_q\eta_q^*+\tfrac{1}{4}B(\eta_q\eta_q^*)^2+\cdots, \tag{5a}$$

$$F_r=\tfrac{1}{2}[A_0'(T-T_0)+\varkappa\eta_0^2]r^2+\tfrac{1}{4}B'r^4+\cdots, \tag{5b}$$

$$F_{r\eta u}=\sum_{i=1}^{3}U_i(a_i\eta_q\eta_q^*+a_i'r^2)+\frac{1}{2}\sum_{i=1}^{6}U_i^2(b_{ii}\eta_q\eta_q^*+b_{ii}'r^2)+\sum_{\substack{i,j=1\\ i\neq j}}^{3}U_iU_j(b_{ij}\eta_q\eta_q^*+b_{ij}'r^2)+\sum_{i=1}^{3}s_iU_ir^2\eta_q\eta_q^*. \tag{5c}$$

Here $A_q=A_0(T-T_0)+D_0(T-T_0)^2-(\kappa-\delta)^2/4\lambda$ corresponds to the incommensurate wave vector $q_\gamma=[(\kappa-\delta)/2\lambda]^{1/2}$, where κ, δ, and λ are the expansion coefficients at the gradient terms,[5] a_i, b_{ij}, and s_i are the corresponding coupling constants. The extraordinary form of A_q is a consequence of the interaction between the order parameters r and η (e_2 and η in the case of Kind and Muralt[5]). It is clear that A_q becames negative only within a certain temperature region $T_c<T<T_i$. The elastic anomalies, which follow from the free-energy expansion (5) can be written as

$$\Delta C_{ij}^*=-4a_i^*a_j^*\eta_0^2\chi_A-4a_i'^*a_j'^*r_0^2\chi_r+b_{ij}\eta_0^2+b_{ij}'r_0^2 \quad (i,j=1-3), \tag{6}$$

$$\Delta C_{66}^*=b_{66}\eta_0^2+b_{66}'r_0^2, \tag{7}$$

where

$$a_i^*=a_i+s_ir_0^2;\quad a_i'^*=a_i'+s_i\eta_0^2, \tag{8}$$

$$\eta_0^2=-A_q/B \quad (T_c<T<T_i),\qquad \eta_0=0 \quad (T<T_c \text{ or } T>T_i), \tag{9}$$

$$r_0^2=-[A_0'(T-T_0)+\varkappa\eta_0^2]/B' \quad (T<T_0),\qquad r_0=0 \quad (T>T_0), \tag{10}$$

$$\chi_A^{-1}=\frac{\partial^2F}{\partial A^*\partial A}[1-i\omega\tau_A]-\frac{i\delta^2\omega\tau_{\text{th}}}{1-i\omega\tau_{\text{th}}}, \tag{11a}$$

$$\chi_r^{-1}=\frac{\partial^2F}{\partial r^2}[1-i\omega\tau_r]-\frac{i\delta'^2\omega\tau_{\text{th}}}{1-i\omega\tau_{\text{th}}}, \tag{11b}$$

$$\delta^2=A_0^2\eta_0^2T/C_\eta;\quad \delta'^2=A_0'^2r_0^2T/C_r.$$

Here η_0 and r_0 are the equilibrium values of the order parameters, C_η and C_r are the specific heat at constant η and r, respectively, A,A^* are the normal phonon coordinates for amplitudon mode (see Dvorak and Petzelt,[9] and Rehwald *et al.*[10]), and ω is the frequency of the dynamical stress. In order to explain ultralow-frequency elastic relaxation, the amplitudon susceptibility χ_A and the order parameter susceptibility χ_r are written in the form of two different relaxational

mechanisms with relaxation times τ_A (or τ_r) and τ_{th}.[11,12] The first part in Eq. (11a) and Eq. (11b) is the so-called Landau-Khalatnikov term which is obtained from a relaxational behavior of the order-parameter fluctuations, i.e., $\delta\eta(t)=\delta\eta(0)\exp(-t/\tau_A)$ and $\delta r(t)=\delta r(0)\exp(-t/\tau_r)$. The second part describes central peak phenomena due to fluctuations of the temperature $\delta T(t)=\delta T(0)\exp(-t/\tau_{th})$ with the thermal diffusion time:[11–13]

$$\tau_{th}=h^2/D\pi^2, \tag{12}$$

where D is the thermal diffusivity constant and h is the thickness of the sample. Since τ_A (τ_r) is usually of the order of 10^{-9}–10^{-13} s and therefore $\omega\tau_A \ll 1$ ($\omega\tau_r \ll 1$) in the region 1–15 Hz, we can neglect the relaxational part of the Landau–Khalatnikov mechanism. On the other hand, the value of τ_{th} is of the order of 0.1–1 s,[12] and therefore the corresponding relaxation contribution should be taken into account. Inserting (11a) and (11b) into Eq. (6) one obtains

$$(T_c<T<T_i),$$

$$\Delta C'_{ij}=\mathrm{Re}(\Delta C^*_{ij})=-\frac{2a_i^*a_j^*}{B}\frac{1+\omega^2\tau_{th}^2k}{1+\omega^2\tau_{th}^2k^2}-\frac{2a_i'^*a_j'^*}{B'}\frac{1+\omega^2\tau_{th}^2k'}{1+\omega^2\tau_{th}^2k'^2}+b_{ij}\eta_0^2+b'_{ij}r_0^2, \tag{13}$$

$$\Delta C''_{ij}=\mathrm{Im}(\Delta C^*_{ij})=\frac{2a_i^*a_j^*}{B}\frac{\omega\tau_{th}(k-1)}{1+\omega^2\tau_{th}^2k^2}+\frac{2a_i'^*a_j'^*}{B'}\frac{\omega\tau_{th}(k'-1)}{1+\omega^2\tau_{th}^2k'^2}, \tag{14}$$

$$(T<T_c \ \text{ or } \ T_i<T<T_0),$$

$$\Delta C'_{ij}=\mathrm{Re}(\Delta C^*_{ij})=-\frac{2a'_ia'_j}{B'}\frac{1+\omega^2\tau_{th}^2k'}{1+\omega^2\tau_{th}^2k'^2}+b'_{ij}r_0^2, \tag{15}$$

$$\Delta C''_{ij}=\mathrm{Im}(\Delta C^*_{ij})=\frac{2a'_ia'_j}{B'}\frac{\omega\tau_{th}(k'-1)}{1+\omega^2\tau_{th}^2k'^2}, \tag{16}$$

where $k=1+A_0^2T/2C_\eta B$ and $k'=1+A_0'^2T/2C_rB'$. Let us now compare Eqs. (13)–(16) with the experimental data. The asymmetric anomalous behavior of the real and imaginary parts of the complex effective elastic constants $C_r^*[100]$ (Fig. 2) and $C_r^*[110]$ (Fig. 3), which is observed near T_i and T_c, follows from the first terms of Eqs. (13) and (14) if we assume that the renormalized coupling constants a_i^* strongly depend on the temperature due to the contribution of the order parameter r_0 ($a_i^*=a_i+s_ir_0^2$). From the experimental data it follows that a_i and s_i should have opposite sign and $|a_i|\approx|s_ir_0^2|$ near T_i. Only in this case the renormalized coupling constants a_i^* are negligibly small in the region of T_i. Therefore the anomalous softening will not appear here, however it should be clearly observed near T_c since the coupling constants a_i^* became remarkable far from T_i.

An unusual global decrease in the imaginary part of both elastic constants $C_r^*([100])$ and $C_r^*([110])$ as well as the clear increase in the real part of $C_r^*([100])$ (see Figs. 2 and 3), which is observed in the whole temperature range of the incommensurate γ phase, immediately follows from the comparison of the second terms in Eqs. (13) and (14) with the first terms in Eqs. (15) and (16), respectively. From the experimental data it follows that $|a_i'^*|=|a_i'+s_i\eta_0^2|<|a_i'|$, therefore if $a_i'>0$, the coupling constants s_i should be negative. In other words, the phase transition into the incommensurate γ phase is accompanied by a decrease of the effective renormalized coupling constant $a_i'^*$ due to the direct negative contribution of the incommensurate modulation amplitude η_0^2. Finally we must stress that all contributions mentioned above strongly depend on the frequency, as follows from the corresponding relaxation parts of Eqs. (13)–(16). Particularly, the anomalies in the imaginary part of C_r^* should be clearly observed only at low frequencies ($\omega\tau_{th}\approx 1/k$; $(1/k')$) while in the high-frequency region ($\omega\tau_{th}\gg 1/k$; $(1/k')$) it gradually vanishes. The anomaly in the real part would remain also at high frequencies, however, it would be less compared to those observed in the low-frequency limit $[\Delta C_r'(\omega=0)/\Delta C_r'(\omega\tau_{th}\gg 1)=k;\ (k')]$. In this picture the obtained experimental results (Figs. 2–5) are in good qualitative agreement with the predictions from the phenomenological theory. One must note that we neglected here the temperature dependences of the thermodynamical coefficients B and B', which from our point of view should be taken into account in the case of a more quantitative description. This remark is especially important in the case of the coefficient B, since the second-order transition at T_i and the first-order transition at T_c are situated on different sides around the hypothetical tricritical point, where this coefficient changes its sign. Particularly, in the region of small B values it is necessary to include into the free energy expansion the sixth-order term $[C(\eta_q\eta_q^*)^3/6]$, which changes the form of Eqs. (13) and (14). However, since the phase transitions at T_i and T_c show clear features of first- and second-order transitions, respectively, it is reasonable to assume that the hypothetical tricritical point ($B=0$) is situated near the middle of the γ phase. In that case Eqs. (13) and (14) are valid for the explanation of the elastic anomalies in the vicinity of both incommensurate phase transition points. Finally we assume that the asymmetrical behavior of the complex effective elastic constant $C_r^*[100]$ and $C_r^*[110]$ observed near T_i and T_c is related only with one or several elastic constants C_{ij}. Unfortunately, from our measurements we cannot determine which elastic constants C_{ij} are responsible for a such unusual elastic behavior in the phase transition region to the upper incommensurate phase. The answer of this question may be obtained from further ultrasonic measurements.

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