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Study of the phason contribution to the acoustic anomaly of C_{55} in incommensurate A_2BX_4-type compounds

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Abstract. Taking account of an Umklapp term in the Landau free energy, we show the splitting of the amplitudon and phason branches. The features and symmetry of the new modes have been derived. Coupling between phase modes and acoustic modes in two A_2BX_4-type crystals has been studied. The downward step observed in the elastic constant C_{55} in the improper ferroelectric K_2SeO_4 near the lock-in phase transition has been attributed to coupling between a transverse acoustic and a high-frequency phason, while the decrease in the same elastic constant in the incommensurate phase of the improper ferroelastic compound TMAT-Cu has been attributed to coupling between a transverse acoustic and a low-frequency phason.

1. Introduction

In what follows we are interested in the phason contribution to the acoustic anomalies of potassium selenate and tetramethylammonium tetrachlorocuprate (TMAT-Cu) which belong to the large incommensurate A_2BX_4 family. The A_2BX_4-type crystals are orthorhombic with space group *Pnam* (D_{2h}^{16}) in the high-temperature phase (normal). On cooling, some of them undergo an incommensurate structural phase transition before becoming ferroelectric or ferroelastic in the commensurate phase (locked). In the group $\{N(CH_3)_4\}_2BCl_4$ the copper compound (TMAT-Cu) shows a particular behaviour. The incommensurate–commensurate transition is ferroelastic (Sawada *et al* 1980a). The elastic constant C_{55} shows a pronounced anomaly in the incommensurate phase (Sawada *et al* 1980b, Rehwald and Vonlanthen 1985). The same elastic constant has a different behaviour near the lock-in phase transition in potassium selenate (Rehwald and Vonlanthen 1981) which is ferroelectric.

Let us summarize some aspects of these two compounds. K_2SeO_4 is the most studied member of the A_2BX_4 family. At $T = T_i$ it undergoes a second-order phase transition induced by a soft phonon (Iizumi *et al* 1977) with wavevector $q_0 = (1 - \delta)a^*/3$. δ decreases with decreasing temperature and vanishes discontinuously at T_1. The crystal then locks into a polar orthorhombic superstructure with the space group $Pna2_1$ (C_{2v}^9). Few experimental studies have been devoted to the study of TMAT-Cu. No phonon softening has been observed and the displacive character of the transition is not established. The parameter δ is almost temperature independent (Gesi and Iizumi 1980) in the incommensurate phase. It vanishes abruptly at T_1. The superstructure of the ferroelastic phase is monoclinic with the space group $P12_1/a1$ (C_{2h}^5). In both crystals the

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lattice parameter along the a axis is tripled in the locked phase. The behaviour of the elastic constant C_{55} in K_2SeO_4 and TMAT-Cu has been interpreted (Rehwald and Vonlanthen 1981, 1985, Lemanov 1986, Sawada *et al* 1980b) in terms of a coupling between the shear deformation e_5 and incommensurate modes with wavevector δa^* without taking into account the existence of a gap at $q_0 \pm \delta a^*$ in the phason and amplitudon branches.

In the next section we show that such acoustic anomalies can be interpreted in the framework of the Landau theory if we take into account Umklapp terms such as $\langle Q(q_0)\rangle^4 Q(q_0+\delta a^*)Q(q_0+\delta a^*)$ in the free-energy expansion. One can also extract, from the fourth-order coupling term between the first- and the second-order parameter (polarization or strain), Umklapp terms equivalent to the above-mentioned term and in which $\langle Q(q_0)\rangle^4$ is replaced by $\langle P(\delta a^*)\rangle\langle Q(q_0)\rangle$. These terms introduce gaps in the phason and amplitudon branches at wavevector δa^*. However, numerical evaluation (Sannikov and Golovko 1984), in the case of K_2SeO_4, shows that the first Umklapp term is the most important. We show also that the instability at $T = T_1$ of the phason belonging to the lower branch with *ungerade* (u) character in the case of K_2SeO_4 and *gerade* (g) character in the case of TMAT-Cu induces a ferroelectric or ferroelastic lock-in phase transition according to its character. Acoustic anomalies induced by the coupling between acoustic modes and phase modes are discussed in section 3. We show particularly that the acoustic anomaly of C_{55} in K_2SeO_4 is mainly due to the behaviour of the phason with wavevector δa^* belonging to the upper branch. It has a B_{2g} symmetry as the shear strain e_5 and is Raman active in the $c(a, c)b$ geometry. The symmetry of phase modes at δa^* is interchanged in the case of TMAT-Cu. The acoustic anomaly of C_{55} in this compound is due to a B_{2g}-type phonon belonging to the lower phason branch.

2. Phonon spectrum

The splitting of the phase mode branch has been treated analytically by McMillan (1977) and Bruce and Cowley (1978). The amplitude mode branch has been neglected by them. We develop below an analytical solution of this problem taking into account the two branches. For this purpose the order parameter is chosen in such a way that it describes the normal–incommensurate transition. Such an order parameter is the normal coordinate of the incommensurate distortion Q_{q_0} belonging to the Σ_2 small group representation, with $q_0 = (1-\delta)a^*/3$. Then the relevant free energy can be written in the form (up to the fourth-order terms)

$$F = \Omega_\eta^2(q_0)Q(q_0)Q^*(q_0) + b[Q(q_0)Q^*(q_0)]^2 \tag{1}$$

with

$$\Omega_\eta^2(q) = a_t(T - T_i) + f_i q_i^2 \qquad q_i = (q \mp q_0)_i.$$

f_i are constants characterizing the soft-mode dispersion surface $\Omega_\eta(q)$ near q_0. T_i is the actual temperature of the normal–incommensurate phase transition. The increase in energy due to the elementary excitations can be written in the diagonalized form

$$\delta F = \tfrac{1}{2}\sum_q [\Omega_A^2(q)A(q)A^*(q) + \Omega_\varphi^2(q)\varphi(q)\varphi^*(q)] \tag{2}$$

in which $\Omega_A(q)$ and $\Omega_\varphi(q)$ are the frequencies of the amplitudon and the phason modes, respectively (Bruce and Cowley 1978):

$$\Omega_A^2(q) = 2b\eta^2 + f_i q_i^2 \tag{3a}$$

$$\Omega_\varphi^2(q) = f_i q_i^2. \tag{3b}$$

$A(q)$ and $\varphi(q)$ are their eigenvectors:

$$A(q) = (1/\eta)[\langle Q(-q_0)\rangle Q(q_0+q) + \langle Q(q_0)\rangle Q(-q_0+q)] \tag{4a}$$
$$\varphi(q) = (1/\eta)[\langle Q(-q_0)\rangle Q(q_0+q) - \langle Q(q_0)\rangle Q(-q_0+q)] \tag{4b}$$

in which $\langle Q(q_0)\rangle = (\eta/\sqrt{2})\exp(\mathrm{j}\theta)$ is the static distortion. Let us derive the symmetry of these modes. The soft-mode coordinates $Q(\mp q_0)$ transform according to the irreducible representation Σ_2 of the point group $C_{2v}(q_0)$. The modes $A(0)$ and $\varphi(0)$ have g and u characters, respectively. The product $\langle Q(q_0)\rangle Q(-q_0)$ (or its conjugate complex) transforms like the identity representation Σ_1 of the point group which is correlated to the irreducible representations B_{3u} and A_g of the normal phase space group D_{2h}^{16}. $A(0)$ and $\varphi(0)$ are of A_g- and B_{3u}-type symmetry, respectively. The analysis of the eigenvectors shows that these branches can be visualized as amplitude and (approximately) phase fluctuations of the primary distortion (Bruce and Cowley 1978).

K_2SeO_4 has a wide temperature range of incommensurate structure. This suggests that the sixth-order terms

$$\frac{1}{6!}\sum_{q_1\ldots q_6} U^{(6)}(q_1,\ldots,q_6)Q(q_1)\ldots Q(q_6)\delta(q_1+\ldots+q_6) \tag{5}$$

in the free-energy expansion of the normal phase (Iizumi *et al* 1977) are small. (As we deal with the single branch Σ_2 the branch index has been omitted; the δ function ensures wavevector conservation modulo a reciprocal lattice vector.) However, in order to explain the anomalous part of the elastic constant C_{55} which occurs near the lock-in phase transition, we need to take them into account under the form

$$\sum_q c(q_0,q_0,q_0,q_0,q_0+K+q,q_0+K-q)\langle Q(q_0)\rangle^4 Q(q_0+K+q)Q(q_0+K-q) + \mathrm{cc} \qquad K=\delta a^* \tag{6}$$

in which four phonon coordinates have been frozen. The anharmonic coefficient c which is a fraction of $U^{(6)}$ is assumed to be q independent. We assume that it is positive. K determines the position in the reciprocal lattice of the satellite reflections. Terms (6) introduce gaps in the amplitudon and the phason branches at $q_0 \pm K$ as we are going to see. Using the eigenmodes $A(q)$ and $\varphi(q)$ (equation (4)), terms (6) can be rewritten as follows:

$$\delta F' = \Delta[A(K+q)A(K-q) + \varphi(K+q)\varphi(K-q)] + \mathrm{cc} \tag{7}$$

with $\Delta = \frac{1}{8}c\eta^4\exp(\mathrm{j}6\theta)$. For simplicity, terms corresponding to the phason–amplitudon interaction energy have been omitted. The total increase in energy can be diagonalized once again. The four dispersion relations of the modes deduced from the dynamical matrix can be written in the condensed form

$$[\Omega_i^{\mp}(\mp K+q)]^2 = \tfrac{1}{2}\{\Omega_i^2(K+q) + \Omega_i^2(-K+q) \mp \sqrt{[\Omega_i^2(K+q) - \Omega_i^2(-K+q)]^2 + 4|\Delta|^2}\}. \tag{8}$$

The + sign refers to the upper branches while the − sign refers to the lower branches. The index i stands for φ or A. The gap in the spectrum at $q_0 \pm K$ is equal to $2|\Delta|$. The eigenvectors of the modes belonging to the lower phason and amplitudon branches are given, respectively, by

$$\varphi^-(q) = (1/\sqrt{2})[\exp(\mathrm{j}3\theta)\,\varphi(K+q) + \exp(-\mathrm{j}3\theta)\,\varphi(-K+q)] \tag{9a}$$
$$A^-(q) = (1/\sqrt{2})[\exp(\mathrm{j}3\theta)\,A(K+q) - \exp(-\mathrm{j}3\theta)\,A(-K+q)] \tag{9b}$$

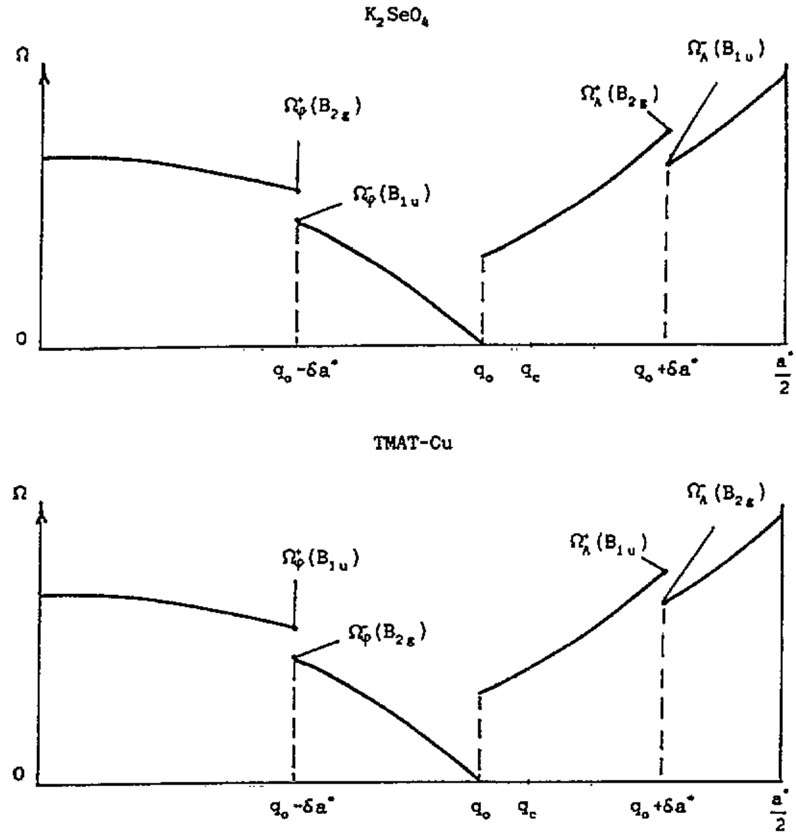

Figure 1. Phonon spectrum in the incommensurate A_2BX_4 compounds. The modes $\varphi^+(\delta a^*)$ and $\varphi^-(\delta a^*)$ have, respectively, B_{2g} and B_{1u} symmetry in the improper ferroelectric K_2SeO_4 and conversely in the improper ferroelastic TMAT-Cu (see also Petzelt (1981)).

while those belonging to the upper branches are given by

$$\varphi^+(q) = (1/\sqrt{2})[\exp(\mathrm{j}3\theta)\varphi(K+q) - \exp(-\mathrm{j}3\theta)\varphi(-K+q)] \qquad (10a)$$

$$A^+(q) = (1/\sqrt{2})[\exp(\mathrm{j}3\theta)A(K+q) + \exp(-\mathrm{j}3\theta)A(-K+q)]. \qquad (10b)$$

The spectrum, showing a single gap in each branch, is schematically represented in figure 1. Passing through the lock-in point transition, K vanishes and the phase variable is fixed. For the special choice $\theta = \frac{1}{6}\pi$, in the locked phase of K_2SeO_4, one can deduce from equations (9) and (10) that the upper amplitudon branch and the lower phason branch disappear from the spectrum.

The phonon spectrum of TMAT-Cu can be deduced from those of K_2SeO_4. Making a change in phase $3\theta \to 3\theta + \frac{1}{2}\pi$ (which corresponds to a change in sign of the coefficient c) in equations (9) and (10), φ^- changes to φ^+ and A^- changes to A^+ and conversely. The symmetry of modes with wavevector δa^*, which is discussed below, will be consequently interchanged in the case of TMAT-Cu. For $\theta = 0$ the lower phason branch and the upper amplitudon branch disappear from the phonon spectrum of the commensurate phase, as in the case of K_2SeO_4.

The symmetry of the new modes at the gap can be deduced as follows. Let us begin with the symmetry of the phason modes in the case of K_2SeO_4. The space group of the normal phase (D_{2h}^{16}) contains the inversion operation. It transforms $Q(q_0)$ into $Q(-q_0)$.

Table 1. The matrices of the representation of the space group *Pnam* with the star $(q_c = \frac{1}{3}a^*, -q_c)$ restricted to the basic translation $a_L = 3a$. The basis consists of two linear combinations of the order parameter components $(1/\sqrt{2})[Q(q_c) + Q(-q_c)]$ and $(1/\sqrt{2})[Q(q_c) - Q(-q_c)]$. $Q(q_c)$ belongs to the Σ_2 irreducible representation of the point group $C_{2v}(q_0)$. The representation is decomposed into two irreducible representations B_{2g} and B_{1u} of the space group. τ_1, τ_2 and τ_3 refer to the fractional translations $\frac{1}{2}(a + b + c)$, $\frac{1}{2}(a + b)$ and $\frac{1}{2}c$, respectively.

	$(E\|0)$	$(C_2^x\|\tau_1)$	$(C_2^y\|\tau_2)$	$(C_2^z\|\tau_3)$	$(I\|0)$	$(\sigma_x\|\tau_1)$	$(\sigma_y\|\tau_2)$	$(\sigma_z\|\tau_3)$
B_{2g} B_{1u}	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$

One can show that $\varphi^-(0)$ has u character while $\varphi^+(0)$ has g character. The symmetry of $\varphi^-(0)$ (equation (9*a*)) depends on the symmetry of the product $\langle Q(q_0)\rangle^3\varphi(K)$ while the symmetry of $\varphi(K)$ (equation (4*b*)) depends on the symmetry of the product $\langle Q(-q_0)\rangle Q(q_0+K)$. This latter transforms under the effect of the symmetry operation R, which leaves q_0 invariant, as

$$D_{\Sigma_2}(R)D_{\Sigma_2}(R)\exp[\mathrm{j}q_0(t+\tau)]\exp[-\mathrm{j}(q_0+K)(t+\tau)] = D_{\Sigma_1}(R)\exp[-\mathrm{j}K(t+\tau)] \tag{11}$$

in which t and τ are the lattice translation and fractional translation, respectively, associated with the rotational symmetry operation R. $D_{\Sigma_i}(R)$ is the character of the representation Σ_i. From (11), one can deduce that $\varphi(K)$ transforms like (Σ_1, K) and consequently $\varphi^-(0)$ transforms like

$$\langle Q(q_0)\rangle^3(\Sigma_1, K). \tag{12}$$

Such a quantity transforms under the effect of the symmetry operation $(R|t+\tau)$ as

$$[\hat{D}_{\Sigma_2}(R)]^3\exp(-\mathrm{j}a^*t) \qquad 3q_0 + \delta a^* = a^*. \tag{13}$$

$\hat{D}_{\Sigma_2}(R)$ is the character of the projective representation associated with R. One can see that $[\hat{D}_{\Sigma_2}(R)]^3\exp(-\mathrm{j}a^*t)$ transforms like the irreducible representation Σ_3 of $C_{2v}^9(q_0)$ which is correlated to the irreducible representation B_{2g} and B_{1u} of the normal phase space group D_{2h}^{16}. Taking account of the character of the phase modes, one can assert that $\varphi^+(0)$ and $\varphi^-(0)$ are of B_{2g}- and B_{1u}-type symmetry, respectively. Following the same procedure, one can find that $A^+(0)$ and $A^-(0)$ are of B_{2g}- and B_{1u}-type symmetry, respectively.

Considering the change in phase $3\theta \rightarrow 3\theta + \frac{1}{2}\pi$, one can find that the phason and amplitudon with wavevectors δa^* belonging to the lower branch are of B_{2g}-type symmetry while those belonging to the upper branch are of B_{1u}-type symmetry. As mentioned above, this situation is realized in TMAT-Cu.

Let us now investigate what type of symmetry the phonons implied in the lock-in phase transformation. For this purpose we refer to a theorem of Landau and Lifshitz (1967). As the space group order $\mathbb{G}_0$ of the normal phase is twice the order of the subgroup $\mathbb{G}$ of the locked phase, it possesses an irreducible representation which induces the totally symmetrical representation of the subgroup $\mathbb{G}$. Using two linear combinations of $Q(q_c, \Sigma_2)$ and $Q(-q_c, \Sigma_2)$ as the basis, one can easily obtain the matrices of representation of the symmetry operations belonging to the space group $\mathbb{G}_0 = Pnam$ (table 1) and show that such representation decomposes into two irreducible representations B_{2g} and B_{1u} of D_{2h}^{16} (first and second lines, respectively, of the diagonalized matrices) which are correlated to the identity representation of C_{2h}^5 and C_{2v}^9, respectively. The direct transition from D_{2h}^{16} to C_{2h}^5 or C_{2v}^9 is due to the mode B_{2g} or B_{1u} respectively. This is in agreement with the symmetry of the amplitude mode which remains in the phonon spectrum of the locked phase and which belongs to the identity representation of the appropriate space group.

3. Elastic anomalies in A_2BX_4 compounds

3.1. *Elastic anomaly in* K_2SeO_4

In this section we are interested in the coupling between the shear deformation and the high-frequency phason in K_2SeO_4 which is assumed to be at the origin of the downward step observed in the elastic constant C_{55} at around the lock-in transition (Rehwald and Vonlanthen 1981, Lemanov *et al* 1986). Group theory shows that the strain e_{xz} interacts with the order parameter through a fourth-order coupling term (Iizumi *et al* 1977)

$$a_5(q_0\Sigma_2, q_0\Sigma_2, q_0\Sigma_2, K\Sigma_3)Q^3(q_0)e_{xz}(K) + \mathrm{cc}. \tag{14}$$

For simplicity the fourth-order anharmonic coupling coefficient will also be assumed to be q independent. The term (14) can be rewritten as follows:

$$\delta F_c = 3a_5\eta^2[\exp(\mathrm{j}2\theta)\, Q(q_0 + K - q)e_{xz}(q)] + \mathrm{cc} \tag{15}$$

in which two phonon coordinates have been frozen. $e_{xz}(q)$ represents the shear wave while the normal coordinates $Q(q_0 + K - q)$ can be expressed in terms of phase and amplitude eigenmodes (equation (4)). The interaction energy can be rewritten as follows:

$$\delta F_c = 3a_5\eta^2\{\exp(\mathrm{j}3\theta)(1/\sqrt{2})[A(K-q) + \varphi(K-q)]\, e_{xz}(q) + \exp(-\mathrm{j}3\theta)(1/\sqrt{2})[A(-K+q) - \varphi(-K+q)]\, e_{xz}(-q)\}. \tag{16}$$

Ultrasonic measurements are made at small wavevectors and the condition $q \ll K$ is realized. In the limit $q = 0$ the high-frequency phason and amplitudon have the same B_{2g} symmetry as e_{xz}. The resulting elastic anomaly of C_{55} is then

$$\Delta C_{55} = -\tfrac{9}{2}a_5^2\eta^4\{1/[(\Omega_\varphi^+(K)]^2 + 1/[(\Omega_A^+(K)]^2\} \qquad T > T_1 \tag{17}$$

with

$$[\Omega_\varphi^+(K)]^2 = |\Delta| + f_1K^2$$

$$[\Omega_A^+(K)]^2 = |\Delta| + 2b\eta^2 + f_1K^2.$$

The high-frequency phason (activated by a three-phonon process) has been observed by means of Raman scattering (Inoue and Ishibashi 1983). The decrease in its frequency as the lock-in phase transition is approached from above is due to the decrease in K. The low-frequency mode observed in infrared spectra (Petzelt *et al* 1979) is the phason with B_{1u} symmetry. The continuity of the amplitude mode frequency is probably due to the small lock-in energy. The hardening of C_{55} below T_l is due to the increase in the $q = 0$ phason frequency (Inoue and Ishibashi 1983).

3.2. *Elastic anomaly in* TMAT-*Cu*

TMAT-Cu is an improper ferroelastic compound. The elastic constant C_{55} shows a clear change in slope at T_i, decreases rapidly within a few kelvins and reaches a minimum in the incommensurate phase (Rehwald and Vonlanthen 1985). The disappearance of C_{55} has been reported by Sawada *et al* (1980b). This behaviour suggests dispersive coupling between an acoustic mode and a low-frequency mode while the narrow stability range of the incommensurate phase (about 6 K) suggests an important sixth-order lock-in energy. The shear mode e_5 couples the low-frequency phason and amplitudon which are of B_{2g}-type symmetry. The resulting acoustic anomaly is

$$\Delta C_{55} = -\tfrac{3}{8}a_5^2\eta^4\{1/[(\Omega_\varphi^-(K)]^2 + 1/[(\Omega_A^-(K)]^2\} \tag{18}$$

with

$$[\Omega_\varphi^-(K)]^2 = -|\Delta| + f_1 K^2$$

$$[\Omega_A^-(K)]^2 = -|\Delta| + 2b\eta^2 + f_1 K^2.$$

In the case of TMAT-Cu, K is temperature independent. The softening of the phason frequency is due to the increase in the gap $|\Delta| \sim \eta^4$. This leads to a decrease in the elastic constant in the incommensurate phase. The minimum is probably due to the relaxational effects which have not been considered here. The hardening of C_{55} suggests that fourth-order coupling between strains and the order parameter involving the square of these parameters could play a role. The Raman spectra have been investigated by Gomez-Cuevas *et al* (1983). No low-frequency phonons, which are of interest to us, were detected.

4. Conclusion

Taking account of an Umklapp term in a Landau-type free energy we have shown the splitting of the phonon spectrum of the incommensurate structure and the symmetry of modes with wavevector δa^*. The theoretical results have allowed us to study acoustic anomalies of C_{55} in K_2SeO_4 and TMAT-Cu. We suggest that the origin of the acoustic anomaly in K_2SeO_4 near the lock-in phase transition is due to the behaviour of the upper phason branch and conversely the same acoustic anomaly in TMAT-Cu is due to the behaviour of the lower phason branch. The model can be extended to other materials and used to study dielectric anomalies.

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