Helvetica Physica Acta
Vol. 46, 1973.

Birkhäuser Verlag Basel

Phonon-Hydrodynamic Description of Structural Phase Transitions

by **H. Beck**
Institute for Theoretical Physics, University of Zurich, Switzerland

and **P. F. Meier**[1])
IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

(28. III. 73)

Abstract. Recent neutron scattering experiments on $SrTiO_3$ and $KMnF_3$ near the structural phase transition have revealed the existence of a strong central peak, besides the soft phonon doublet at Q_R, the R corner of the Brillouin zone. Starting from a model Hamiltonian for the soft mode an expression for the structure factor $S(k, \Omega)$ is derived. We use the microscopic theory of phonon interactions which leads to the form of S expected from the elastic continuum theory, and can account for a central peak at $k \approx 0$ near phase transitions. The special form of the dispersion curve of the soft mode implies that for $k \approx Q_R$ the same collision processes are dominant as for $k \approx 0$. The resulting structure of $S(k, \Omega)$ for k near Q_R is the same as for $k \approx 0$ which yields a microscopic justification of the hydrodynamic description of the central peak at the R corner.

I. Introduction

The perovskites ABC_3 show a phase transition where the high-temperature cubic phase goes over into a phase of lower symmetry. For $SrTiO_3$, $KMnF_3$, and $LaAlO_3$ this displacive transition is connected with a phonon instability at the R corner of the Brillouin zone where the frequency of one of the R_{25} modes goes to zero for $T \to T_c$ and consists of alternate rotations of the BC_6 octahedra around the cubic axes as revealed in EPR measurements by Müller et al. [1]. Pytte and Feder [2] have shown that the essential features of the transition can be accounted for by considering only the three phonon modes corresponding to these rotations. In subsequent papers they also treated the coupling to other phonon modes, especially the acoustic branches, but the picture of the phase transition driven by the 'soft mode' has not been altered.

Recently, neutron-scattering experiments on $SrTiO_3$ and $KMnF_3$ [3] have revealed an interesting new feature: for T approaching T_c from above and for wave vectors $\vec{k}$ near $\vec{Q}_R$, the R corner of the Brillouin zone, the structure factor $S(\vec{k}, \Omega)$, exhibits a strong peak at $\Omega = 0$ besides the two soft-mode resonances. Such a central peak usually occurs near first-order transitions for $\vec{k} \approx \vec{0}$, representing scattering from long-wavelength critical fluctuations. It was, however, surprising to detect a central peak near a corner of the zone.

---

[1]) IBM Postdoctoral Fellow of the Institute for Theoretical Physics, University of Zurich, Switzerland.

It is well known that the structure factor has the form

$$S(\vec{k},\Omega)=\frac{k_B T}{\Omega}\,\mathrm{Im}\,\frac{1}{\Omega^2-\omega_{\vec{k}}^2-\sigma(\vec{k},\Omega)}. \tag{1}$$

Several attempts have been made to find a form of the self-energy $\sigma(\vec{k},\Omega)$ which would give rise to a central peak in addition to the phonon poles near $\pm\omega_{\vec{k}}$.

Shirane and Axe [4] have reported on the occurrence of a central peak at the structural phase transition in the high-temperature superconductor Nb_3Sn where an acoustic shear mode becomes soft. There a central peak at the center of the Brillouin zone shows up in the response function. Shirane and Axe demonstrated that a complex self-energy of the form

$$\sigma(\vec{k},\Omega)=i\Omega\sigma'-\frac{i\Omega\delta^2}{i\Omega-\gamma} \tag{2}$$

accounts for the observed central peak and the phonon resonances and they showed that expression (2) results from a transition of the usual collision-free to the collision-dominated regime near the phase transition.

For a discussion of the central peak in $SrTiO_3$ where a form of σ analogous to (2) but for k near Q_R is required, several semi-phenomenological theories have recently been proposed. Schwabl [5] used a dynamic theory based on Mori's theory of 'Brownian motion' relating in this way the dynamic quantities to static susceptibilities. Schneider [6] treated $S(\vec{k},\Omega)$ by means of Mori's continued fraction method and obtained an expression for σ in accordance with the moment sum rules. The form of $S(\vec{k},\Omega)$ with the self-energy (2) agrees with the expression derived from the elastic equations [see equation (21)], and leads to a strong central resonance provided that

$$\delta^2 \gg \omega_{\vec{k}}^2. \tag{3}$$

This condition is equivalent to the fact that the ratio of the isothermal and the adiabatic susceptibilities is much larger than unity, which was used by Feder [7] to explain a central peak.

On a more microscopic level, the critical behavior of $SrTiO_3$ can be studied by using a single-mode Hamiltonian of our form (4) as a model for the R_{25} mode that becomes soft. Silberglitt [8] used a quartic anharmonicity to calculate $\sigma(\vec{k},\Omega)$ in a self-consistent way. Enz [9] has pointed out a remarkable property of the dispersion curve of this mode: for $T \gtrsim T_c$ it consists of two almost symmetric branches (see Fig. 1). As a consequence, he sums up the infinite set of 'chain diagrams' which leads to an expression for $\sigma(\vec{k},\Omega)$ reducing to (2) for small Ω.

The lattice dynamic description of the collision-dominated hydrodynamic regime ($\Omega \to 0$, $\vec{k} \to \vec{0}$) is well established: Kadanoff and Martin [10] have shown that the hydrodynamic equations for fluids or elastic solids lead to the form (21) of the structure factor. In lattice dynamics it has been possible to derive this form starting from an anharmonic Hamiltonian (see Refs. [11], [12], and [13]). Sham [11] has pointed out that in this regime ($\vec{k} \approx 0$, $\Omega \approx 0$) perturbation theory breaks down due to hydrodynamic singularities. In this case a Boltzmann equation has to be solved which amounts to summing up the 'ladder graphs'. This procedure gives a microscopic justification for the result of hydrodynamics.

In this work we show that the same microscopic considerations can be made to explain the central peak found at $\vec{k} \approx \vec{Q}_R$ in connection with structural phase transitions. The crucial point is that the above-mentioned symmetry property of the phonon branch also leads to hydrodynamic singularities for this case. Thus for $T \to T_c$ the behavior of $S(\vec{k}, \Omega)$ for $\vec{k} \approx \vec{Q}_R$ and $\Omega \approx 0$ is also governed by hydrodynamic equations.

In this way we get a *microscopic* explanation of the form (2) of the structure factor. Our derivation is based on the same assumptions as the work of Enz [9]. The results of Enz are rederived in a different manner, but in addition it is shown that with the same assumptions also a collision-dominated situation may give rise to the form (2) of σ. This latter case constitutes for $k \approx Q_R$ the analog to the explanation of Axe and Shirane [4] for the central peak in Nb_3Sn at $k \approx 0$.

In Section II the equations of motion for suitable Green's functions are derived starting from a Hamiltonian with cubic and quadratic anharmonicities. In Section III we make use of the hydrodynamic singularities for $\vec{k} \approx \vec{Q}_R$ to transform the integral equation for the vertex part into a generalized Boltzmann-type equation which sums up chain and ladder graphs. The structure factor resulting from this equation is evaluated in the fourth section. Its general form is the same as for $\vec{k} \approx \vec{0}$. Some modifications may, however, arise from the details of the actual dispersion curve. Finally, Section V is devoted to a discussion of the form of the central peak.

II. Hamiltonian and Equations of Motion

We start from the single-mode Hamiltonian

$$H = \tfrac{1}{2} \sum_k B_k^+ B_k + \sum_{\nu=2}^{4} \frac{1}{\nu!} \sum_{k_1 \ldots k_\nu} V_\nu(k_1, \ldots, k_\nu)\, A_{k_1} \ldots A_{k_\nu}. \tag{4}$$

As usual, the operators A_k and B_k are Fourier transforms of the displacements and the momenta of the particles and satisfy

$$[A_k, B_{k'}] = \delta_{kk'}^+. \tag{5}$$

The important information about the behavior of the system is contained in the functions

$$d(k,t) = \langle A_k(t) \rangle \tag{6}$$

and

$$g^r(k, t-t') = \theta(t-t') \langle [A_k(t), A_k^+(t')] \rangle \tag{7}$$

$$= \int \frac{d\omega}{2\pi}\, e^{-i\omega(t-t')} g^r(k, \omega),$$

the bracket denoting a thermal average. The expectation value $\langle A_k(t) \rangle$ corresponds to the order parameter and has the form

$$\begin{aligned} d(k,t) &= 0 && \text{for} \quad T > T_c \\ d(k,t) &= a(T)\, \delta_{k, Q_R} && \text{for} \quad T < T_c. \end{aligned} \tag{8}$$

The retarded commutator g^r determines the structure factor $S(k,\Omega)$:

$$S(k,\Omega) = \mathrm{Im}\, g^r(k,\Omega) \frac{1}{e^{\beta\Omega} - 1} \tag{9}$$

with

$$\beta = (k_B T)^{-1}. \tag{10}$$

For high temperatures where $\Omega \ll \beta^{-1}$ this can be simplified to

$$S(k,\Omega) = \frac{k_B T}{\Omega} \mathrm{Im}\, g^r(k,\Omega). \tag{11}$$

This quantity is best calculated by solving the equations of motion for the imaginary-time Green's function

$$G(k,\tau-\tau') = \frac{1}{i}\langle T_\beta(A_k(\tau)\, A_k^+(\tau'))\rangle, \tag{12}$$

where T_β orders the times from 0 to $-i\beta$. g^r is then related to the Fourier coefficient

$$G(k,z_\nu) = \int_0^{-i\beta} d\tau\, e^{-iz_\nu \tau} G(k,\tau), \quad z_\nu = \frac{2\pi\nu}{-i\beta} \tag{13}$$

by the well-known equation [14]

$$g^r(k,\Omega) = G(k, z = \Omega + i\delta). \tag{14}$$

The technique of functional derivation with respect to an external source has been used in Ref. [12] to derive a system of equations determining G. They read

$$-\frac{\partial^2 G(k,\tau)}{\partial\tau^2} = \delta(\tau) + \int_0^{-i\beta} d\tau'\, \sigma(k,\tau-\tau')\, G(k,\tau'), \tag{15}$$

where the self-energy

$$\sigma(k,\tau) = \sigma_0(k)\, \delta(\tau) + \sigma_F(k,\tau) \tag{16}$$

is given by

$$\sigma_0(k) = V_2(-k,k) + \frac{i}{2}\sum_{k'} V_4(-k,k,k',-k')\, G(k',\tau=0), \tag{17}$$

and

$$\sigma_F(k,\tau) = \frac{i}{2}\sum_{k_1 k_2} V_3(-k,k_1,k_2)\, F(k_1,k_2,k';\tau,\tau). \tag{18}$$

The vertex part F obeys the integral equation

$$F(k,k',k'';\tau-\tau') = \int_0^{-i\beta} d\tau_1\, d\tau_2\, G(k,\tau-\tau_1)\, G(k',\tau'-\tau_2)\,[V_3(-k,k',k'')\,\delta(\tau_1)\,\delta(\tau_2)$$

$$+\frac{i}{2}\sum_{k_1,k_2} V_4(-k,k',k_1,-k_2)\, F(k_1,k_2,k'';\tau_1,\tau_2)\,\delta(\tau_1-\tau_2)$$

$$+ i \sum_{k_1 \ldots k_3} V_3(-k,k_1,k_2)\, V_3(k',-k_3,-k_1)\, G(k_1;\tau_1-\tau_2)$$

$$\times F(k_2,k_3,k'';\tau_1,\tau_2)]. \tag{19}$$

These equations are correct up to terms of the order of V_3^2 and V_4.

In lattice dynamics these equations are well known. If the vertex part is approximated by the first term of (19) the solution of (15) yields information about the frequencies and life-times of phonons with thermal wave vectors k. For long wavelengths, i.e., for wave vectors k near the center of the Brillouin zone, this procedure does not lead to the form of the structure factor $S(k,\Omega)$ expected from hydrodynamics, see for example Ref. [15]. Sham [11] has shown that this is due to 'hydrodynamic singularities' which make a perturbative treatment of (19) in powers of V_3 impossible. In the picture of phonon–phonon interactions these singularities occur since in the three-phonon processes

$$k \leftrightarrows q_1 + k; -q_1 \tag{20}$$

the thermal phonons with wave vectors $-q_1$ and $q_1 + k$ have almost the same energy. Equation (19) can in this case be transformed into a linearized Boltzmann equation (see Refs. [11] and [12]). The solution of the latter, inserted into the self-energy (17) and (18) produces the hydrodynamic form of $S(k,\Omega)$:

$$S(k,\Omega) = \frac{k_B T}{\Omega}\,\mathrm{Im}\,\frac{1}{\Omega^2 - c_T^2 k^2 + i\Omega k^2 \eta - B\dfrac{\Omega k^2}{\Omega + iDk^2}}\,. \tag{21}$$

This structure of S corresponds to the macroscopic elastic equations. It describes a diffusive central peak and the Brillouin doublet, i.e., two propagating sound modes, whose frequencies are renormalized from $\pm c_T k$ to $c_{ad} k$; c_T and c_{ad} being the isothermal and the adiabatic sound velocities, respectively. This renormalization occurs since the form for σ inserted into (21) is appropriate for the collision-dominated regime. The significance of parameters B and D will be discussed in Section IV.

Recent experiments have proved the existence of a strong central peak for $k \approx Q_R$. In the next section we want to show that under certain conditions on the phonon spectrum which seem to be fulfilled in $SrTiO_3$ and $KMnF_3$ for $T \gtrsim T_c$, the three phonon processes (20) again lead to a hydrodynamic singularity, in this case for $k \approx Q_R$, in a similar way as they do for $k \approx 0$ in usual hydrodynamics.

III. Hydrodynamic Singularities in the Vertex Part

Equation (19) for the vertex part F is now treated in the same way as in Ref. [12]. For the sake of completeness some arguments are collected in the Appendix. The

non-instantaneous part σ_F of the self-energy for a phonon with wave vector $Q_R - Q$ near the R corner can be written as

$$\sigma_F(Q_R - Q, \Omega + i\delta) = \frac{i}{2} \sum_q V_3(-Q_R + Q, q, Q_R - Q - q)$$

$$\times \int \frac{d\nu}{2\pi} \left\{ \left[N_0\left(\nu + \frac{\Omega}{2}\right) - N_0\left(\nu - \frac{\Omega}{2}\right) \right] F\left(q, q - Q_R + Q,\right.\right.$$

$$\left. \times Q_R - Q; \nu + \frac{\Omega}{2} + i\epsilon, -\nu + \frac{\Omega}{2} + i\delta \right) + N_0\left(\nu - \frac{\Omega}{2}\right)$$

$$\times F\left(\ldots, \nu + \frac{\Omega}{2} + i\delta, -\nu + \frac{\Omega}{2} - i\epsilon\right) - N_0\left(\nu + \frac{\Omega}{2}\right)$$

$$\left. \times F\left(\ldots, \nu + \frac{\Omega}{2} - i\epsilon, -\nu + \frac{\Omega}{2} + i\delta\right) \right\}, \tag{22}$$

whereas F obeys an equation of the type

$$F\left(q, -Q_R + Q + q, Q_R - Q; \nu + \frac{\Omega}{2} + i\epsilon_1, -\nu + \frac{\Omega}{2} + i\epsilon_2\right)$$

$$= G\left(q, \nu + \frac{\Omega}{2} + i\epsilon_1\right) G\left(q - Q_R + Q, \nu - \frac{\Omega}{2} - i\epsilon_2\right) M(q, Q_R - Q; \nu, \Omega; \epsilon_1, \epsilon_2). \tag{23}$$

Here the ϵ_i are small positive or negative quantities and M is an expression derived from (A2), involving V_3, V_4, G and again the unknown function F. The behavior of F, which for small Q and Ω depends strongly on the signs of ϵ_1 and ϵ_2, can be investigated by examining the product of the two G's on the right-hand side of (23). For those momenta q which will be important in the sum (22) the phonon propagator G can be written as

$$G(k, \omega + i\epsilon) = \frac{1}{\omega^2 - \omega_k^2 + \frac{i}{2} \operatorname{sgn} \epsilon \cdot \Gamma(k, \omega)}. \tag{24}$$

$\Gamma(k, \omega) = -\Gamma(k, -\omega)$ is the imaginary part of the self-energy, whereas the real part has been incorporated into the renormalized ('experimental') phonon frequency ω_k. Using

$$G_1 G_2 = (G_2^{-1} - G_1^{-1})^{-1} (G_1 - G_2) \tag{25}$$

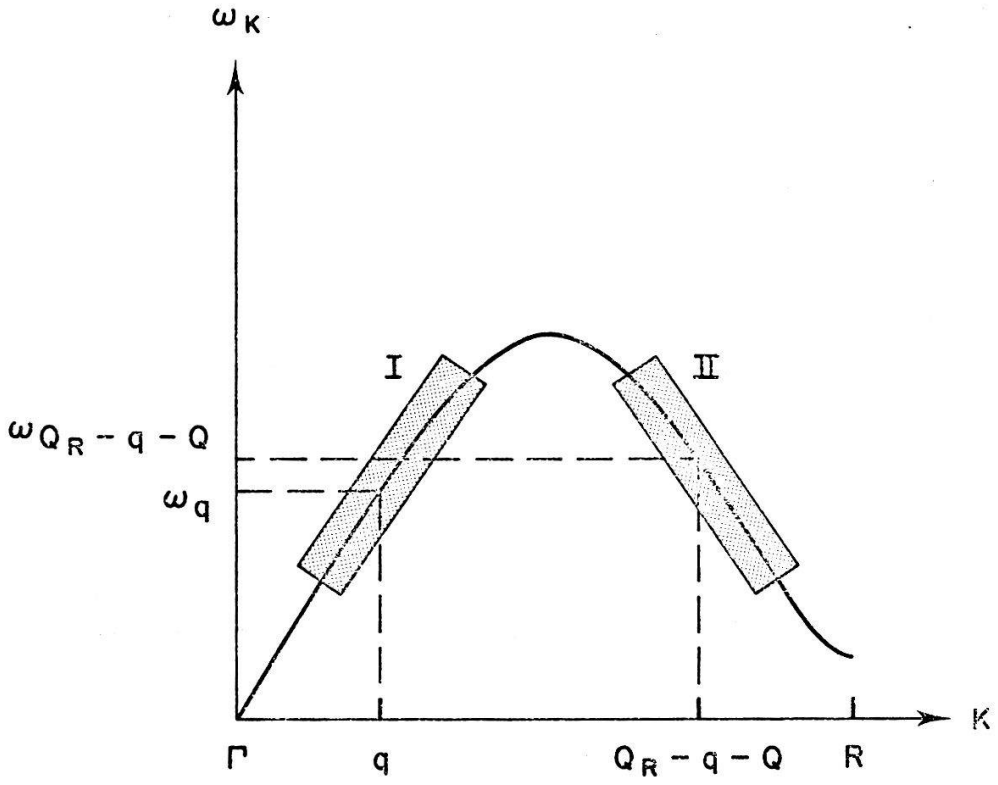

Figure 1
Dispersion curve ω_k of the soft mode in the (1,1,1)-direction as measured by Refs. [16] and [17]. In the hatched areas I and II the phonon energies ω_q and ω_{Q_R-q-Q} are almost equal.

we write

$$G\left(q, \nu+\frac{\Omega}{2}+i\epsilon_1\right) G\left(q-Q_R+Q, \nu-\frac{\Omega}{2}-i\epsilon_2\right)$$

$$= \left[-2\nu\Omega - (\omega^2_{q-Q_R+Q} - \omega_q^2) - \frac{i}{2}\left(\operatorname{sgn}\epsilon_1 \Gamma\left(q, \nu+\frac{\Omega}{2}\right)\right.\right.$$

$$\left.\left. + \operatorname{sgn}\epsilon_2 \Gamma\left(q-Q_R+Q, \nu-\frac{\Omega}{2}\right)\right)\right]^{-1} \left[G\left(q, \nu+\frac{\Omega}{2}+i\epsilon_1\right)\right.$$

$$\left. - G\left(q-Q_R+Q, \nu-\frac{\Omega}{2}-i\epsilon_2\right)\right]. \tag{26}$$

At this stage we follow the argument put forward by Enz [9] which makes use of a special property of the frequencies ω_k of the soft mode treated in our model. The measured dispersion curve [16, 17] for the R_{25} mode in $SrTiO_3$ and $KMnF_3$ shows at $T \gtrsim T_c$ an approximate symmetry as shown in Figure 1. For an appreciable range (areas I and II in Fig. 1) the energies ω_q and ω_{Q_R-q-Q} are almost equal provided Q is very small. Quantitatively, we may write

$$\omega_{Q_R-q} = \omega_q + \Delta(q), \tag{27}$$

expecting $\Delta(q)$ to be very small compared to ω_q. Similarly, we assume

$$\Gamma(q-Q_R,\nu)=\Gamma(q,\nu)+\gamma(q), \tag{28}$$

$\gamma(q)$ again being very small. Thus for the important q values the propagators for phonons with momenta q and Q_R-q can both be written as

$$G(Q_R-q,\omega)\approx G(q,\omega)=\frac{1}{\omega^2-\omega_q^2+i/2\,\mathrm{sgn}\,\epsilon\Gamma(q,\omega)}. \tag{29}$$

An expansion of (26) with respect to the small quantities Ω, Q, $\Delta(q)$ and $\gamma(q)$ yields

$$\begin{aligned}X&=G\left(q,\nu+\frac{\Omega}{2}+i\epsilon_1\right)\cdot G\left(q-Q_R+Q,\nu-\frac{\Omega}{2}-i\epsilon_2\right)\\&\approx\left[-2\nu\Omega+2\omega_q(Q\cdot V_q-\Delta(q))-\frac{i}{2}(\mathrm{sgn}\,\epsilon_2+\mathrm{sgn}\,\epsilon_1)\,\Gamma(q,\nu)-\frac{i}{2}\mathrm{sgn}\,\epsilon_2\,\gamma(q)\right]^{-1}\\&\times\left\{[G(q,\nu+i\epsilon_1)-G(q,\nu-i\epsilon_2)]+\left[2\nu\Omega-2\omega_q(QV_q-\Delta(q))-\frac{i}{2}\gamma(q)\right]\right.\\&\left.\times\frac{\partial G(q,\nu-i\epsilon_2)}{\partial\omega_q^2}+\ldots\right\}.\end{aligned} \tag{30}$$

For $\epsilon_1>0$ and $\epsilon_2>0$ the right-hand side of (30) now shows a hydrodynamic singularity

$$X_{\epsilon_i>0}\approx\frac{\chi(q,\nu)}{-2i\nu\Omega+2i\omega_q(QV_q-\Delta(q))+\Gamma(q,\nu)+\frac{1}{2}\gamma(q)}, \tag{31}$$

whereas for $\epsilon_1\gtrless 0$ and $\epsilon_2\lesseqgtr 0$,

$$X'\approx\frac{\partial G(q,\nu\mp io)}{\partial\omega_q^2}. \tag{32}$$

Here we have defined the spectral function

$$\chi(q,\nu)=i[G(q,\nu+io)-G(q,\nu-io)] \tag{33}$$

and the group velocity

$$V_q=\frac{\partial\omega_q}{\partial q}. \tag{34}$$

Inspection of (23) shows that the hydrodynamic singularity shows up in $F(\ldots;\nu+\Omega/2+io,-\nu+\Omega/2+io)$, whereas $F(\ldots;\pm io,\mp io)$ behaves regularly for Q and Ω going to zero. This part of F is thus replaced by the inhomogeneous term of (23) when inserted into (22). For the singular part

$$F^+(q,Q;\nu,\Omega)=F\left(q,q-Q_R+Q,Q_R-Q;\nu+\frac{\Omega}{2}+io,-\nu+\frac{\Omega}{2}+io\right) \tag{35}$$

we make the ansatz

$$F^+(q,Q;\nu,\Omega) = \chi(q,\nu)\, h(q,Q;\nu,\Omega) \tag{36}$$

and write down (23) explicitly, omitting, however, the regular part of F in the expression for M:

$$\begin{aligned}
&[-2i(\nu\Omega - \omega_q Q V_q + \omega_q \Delta(q) + \Gamma(q,\nu) + \gamma(q))]\, h(q,Q;\nu,\Omega) \\
&= V_3(-q, q-Q_R+Q, Q_R-Q) + \frac{i}{2}\sum_{q'} V_4(-q, q-Q_R+Q, q', Q_R-Q-q') \\
&\quad \times \int \frac{d\omega}{2\pi}\left[N_0\left(\omega+\frac{\Omega}{2}\right) - N_0\left(\omega-\frac{\Omega}{2}\right)\right]\chi(q',\omega)\, h(q',Q;\omega,\Omega) \\
&\quad + \sum_{q'q''} V_3(-q,q',q'')\, V_3^*(q'', q'-Q_R+Q, Q_R-Q-q) \\
&\quad \times \int \frac{d\omega}{2\pi} N_0(\omega)\,[\chi(q'',\omega)\,\chi(q',\omega+\nu)\, h(q',Q;\omega+\nu,\Omega) \\
&\quad + \chi(q'',\nu-\omega)\,\chi(q',\omega)\, h(q',Q;\omega,\Omega)].
\end{aligned} \tag{37}$$

In the following we expect that the spectral function $\chi(q,\nu)$ for the 'thermal' phonons can be represented by two sharp peaks,

$$\chi(q,\nu) \approx \frac{\pi}{\omega_q}[\delta(\nu-\omega_q) - \delta(\nu+\omega_q)]. \tag{38}$$

In accordance with the symmetry between regions I and II of the dispersion curve (Fig. 1) we also assume the anharmonic coupling parameters to be almost equal:

$$V_3(q'', q'-Q_R+Q, Q_R-Q-q) \approx V_3(q'', q', -q). \tag{39}$$

This enables us to proceed in the same way as the usual phonon hydrodynamics was established in Refs. [11] and [12]. Defining

$$\varphi(q,Q,\Omega) = h(q,Q;\nu=\omega_q,\Omega) \tag{40}$$

and integrating (37) over ν from 0 to ∞ we end up with

$$\begin{aligned}
&\left[-i\Omega + iQ\cdot V_q - i\Delta(q) + \frac{\gamma(q)}{2\omega_q}\right]\varphi(q,Q,\Omega) \\
&= \frac{1}{2\omega_q} V_3(-q, q-Q_R+Q, Q_R-Q) + L[\varphi(q,Q,\Omega)] - i\Omega\sum_{q'} J(q,q')\,\varphi(q',Q,\Omega).
\end{aligned} \tag{41}$$

Besides two additional terms on the left-hand side this is a generalized linear Boltzmann equation. The collision operator L which has the same form as in Refs. [11] and [12] is the sum of $\Gamma(q,\nu)$ and the last term of (37). The function

$$J(q,q') = \frac{m(\omega_{q'})}{4\omega_q\,\omega_{q'}} V_4(-q,q,q',-q') \tag{42}$$

with

$$m(x) = \beta N_0(x)\,(N_0(x)+1) \tag{43}$$

corresponds to the quasi-particle interaction first introduced by Göetze and Michel [13].

By means of equations (14) to (18) and (22) the structure factor (11) can now be represented in the form

$$S(Q_R - Q, \Omega) = \frac{k_B T}{\Omega} \operatorname{Im} \frac{1}{\Omega^2 - [A(Q_R - Q) + B(Q_R - Q) - D(Q_R - Q)] + C(Q_R - Q, \Omega)}. \tag{44}$$

Here

$$A(Q_R - Q) = V_2(Q_R - Q, Q - Q_R) \tag{45}$$

is the 'harmonic' frequency and

$$B(Q_R - Q) = \sum_{q'} V_4(-Q_R + Q, q', -q', Q_R - Q)\,\frac{N_0(\omega_q) + 1/2}{2\omega_q} \tag{46}$$

is the first term of the usual self-consistent phonon approximation [3, 18]. D is calculated by inserting the lowest-order value of the regular part of F into (22):

$$D(Q_R - Q) = \sum_{q} |V_3(q, -Q_R + Q, Q_R - Q - q)|^2 \left[\frac{N_0(\omega_q) + 1/2}{4\omega_q^3} + \frac{m(\omega_q)}{4\omega_q^2}\right]. \tag{47}$$

C finally contains the solution of the transport equation (41):

$$C(Q_R - Q, \Omega) = -i\Omega \sum_{q} \frac{1}{2\omega_q} V_3(q, -Q_R + Q, Q_R - Q - q)\, m(\omega_q)\, \varphi(q, Q, \Omega). \tag{48}$$

IV. Evaluation of $S(Q_R - Q, \Omega)$

The symmetry property of the dispersion curve has led to a hydrodynamic equation determining the structure factor for wave vectors in the neighborhood of the R corner. Now we want to investigate the form of the term C in (44) by solving the collision equation (41) in some approximation. To this end the wave-vector dependence of V_3 and V_4 can qualitatively be represented as

$$V_3(-q, q - Q_R + Q, Q_R - Q) \approx g_3\, \omega_q^2\, \alpha(Q_R - Q) \tag{49}$$

$$V_4(q', -q', Q_R - Q, Q - Q_R) \approx g_4\, \omega_q^2,\, \alpha^2(Q_R - Q), \tag{50}$$

where g_ν are anharmonic coupling constants and $\alpha(Q_R - Q)$ will be discussed later on. These approximations are certainly justified as we do not calculate the effects of the anharmonic coupling parameters quantitatively.

Two limiting cases can now be treated in a simple manner:

i) The collision operator is replaced by a relaxation time $\tau(q)$, whereas the quasi-particle interaction J is retained. This corresponds to the summation of the 'chain'

diagrams performed by Enz [9] and leads to the form

$$C_1(Q_R - Q, \Omega) = \frac{g_3^2}{g_4} \alpha^2(Q_R - Q) \frac{\Omega}{\Omega - \frac{4i}{g_4 Z}}. \tag{51}$$

The function

$$Z(Q, \Omega) = \sum_q \frac{m(\omega_q)\, \omega_q^2}{-i\Omega + iQV_q - i\Delta(q) + \frac{\gamma(q)}{2\omega_q} + \frac{1}{\tau(q)}} \tag{52}$$

is still Ω- and Q-dependent. For small Q and Ω it can be replaced by $Z(0,0)$. This description applies to the collisionless regime.

ii) If the collision term L dominates, J can be neglected and the Boltzmann equation can be solved starting from the 'hydrodynamic' eigenfunctions of L (collision invariants) and treating the drift term as well as the term $-i\Delta(q) + \gamma(q)/2\omega(q)$ as a perturbation. Details of such a procedure are given in Ref. [19] and in Section 8 of Ref. [12]. The resulting expression for C reads

$$C_2(Q_R - Q, \Omega) = \frac{\Omega U(Q_R - Q)}{\Omega + i\Lambda(Q)} \tag{53}$$

with

$$U(Q_R - Q) = \frac{g_3^2}{4} \alpha^2(Q_R - Q) \sum_q \omega_q^2 m(\omega_q) \tag{54}$$

and

$$\Lambda(Q) = -Q^2 \frac{\langle (QV_q)^2 \rangle}{\langle QV_q\, LQV_q \rangle} - i\langle \Delta(q) \rangle + \left\langle \frac{\gamma(q)}{2\omega_q} \right\rangle. \tag{55}$$

The brackets denote the following average:

$$\langle f(q) \rangle = \frac{\sum_q m(\omega_q)\, \omega_q f(q)\, \omega_q}{\sum_q \omega_q^2 m(\omega_q)}. \tag{56}$$

C_1 and C_2 have the same analytic structure. C_1 corresponds to the solution of the Boltzmann equation in the collisionless domain, whereas C_2 is closely related to the results of usual phonon hydrodynamics. There only the first contribution to $\Lambda(Q)$ is present, which, in accordance with the hydrodynamic equations has to be identified as

$$\frac{\langle (QV_q)^2 \rangle}{\langle QV_q\, LQV_q \rangle} = -\frac{\kappa}{C_v}, \tag{57}$$

κ being the thermal conductivity of the system. Some expressions showing up in $U(Q_R - Q)$ can also be identified with thermodynamic quantities. In the picture of renormalized phonons the quasi-harmonic free energy is known to be

$$F_{qh} = k_B T \sum_q \log \left[2 \sinh \left(\frac{\omega_q}{2k_B T} \right) \right], \tag{58}$$

ω_q being the 'experimental' phonon frequencies depending on the lattice constant a. The specific heat at constant volume

$$C_v = -T \frac{\partial^2 F_{qh}}{\partial T^2}$$

and the tension coefficient

$$\lambda = \frac{\partial^2 F_{qh}}{\partial T \, \partial a}$$

can then be put into the following form (see Ref. [13]):

$$C_v = \frac{1}{T} \sum_q m(\omega_q) \, \omega_q^2 \tag{59}$$

and

$$\lambda = \frac{g_3}{2T} \sum_q m(\omega_q) \, \omega_q^2. \tag{60}$$

Thus we can identify

$$U(Q_R - Q) = \alpha^2(Q_R - Q) \frac{T\lambda^2}{C_v} \tag{61}$$

and end up with

$$S(Q_R - Q, \Omega) = \frac{k_B T}{\Omega} \operatorname{Im} \frac{1}{\Omega^2 - \chi_T^{-1}(Q_R - Q) + C_2(Q_R - Q, \Omega)}, \tag{62}$$

where

$$C_2(Q_R - Q, \Omega) = \frac{\alpha^2(Q_R - Q) \, \lambda^2 \, \Omega T}{C_v \left(\Omega + iQ^2 \frac{\kappa}{C_v} + i \left\langle \frac{\gamma}{2\omega} \right\rangle + \langle \Delta(q) \rangle \right)}. \tag{63}$$

Here we have introduced the static isothermal susceptibility $\chi_T(k)$ of the system with respect to an external force conjugate to the dynamic variable A_k. It is given by

$$\begin{aligned} \chi_T(k) &= -\lim_{\Omega \to 0} g^r(k, \Omega) \\ &= [A(k) + B(k) - D(k)]^{-1}. \end{aligned} \tag{64}$$

In the derivation of solution (53) of the Boltzmann equation a regular term arising from the eigenfunctions of L with non-vanishing eigenvalues has been omitted. It would have led to a further contribution to C_2 of the form

$$C_2^{(\mathrm{reg})}(Q, \Omega) = i\Omega\eta\alpha^2(Q_R - Q). \tag{65}$$

In analogy to the hydrodynamic form (21) of $S(k, \Omega)$, where $\alpha^2(Q_R - Q)$ is proportional to Q^2, η can be identified with a viscosity. The above identifications with thermodynamic quantities should, however, be considered with precaution: λ, C_v, χ_T and κ are

quantities belonging to the single mode of our model. They may differ appreciably from the values for the crystal as a whole. One would, however, expect that the critical behavior of these quantities is mainly determined by the contributions stemming from the soft mode alone.

V. Discussion

It has already been mentioned in Section IV that solutions (51) and (53) for the term $C(k,\Omega)$ in the structure factor both have the same form although they result from different microscopic mechanisms, namely, the quasi-particle interaction and the phonon–phonon collisions, respectively. For wave vectors $k \approx 0$ it is the form C_2 in (53) emerging from the treatment of collisions that produces the correct hydrodynamic result (21) for the phonon propagator (see Ref. [15]). This fact leads to the identification of some of the contributions to C_2 with thermodynamic quantities. In the following we shall restrict our discussion to C_2, i.e., to result (63).

The term C has its origin in anharmonic interactions. In 'normal' situations where the two main poles of $S(k,\Omega)$ describe propagating phonons it is small in the sense that

$$\frac{\lambda^2 T}{C_v}\alpha^2(Q_R - Q) \ll \chi_T^{-1}(Q_R - Q). \tag{66}$$

It shifts the isothermal phonon frequency $\chi_T^{-1/2}$ to $\chi_s^{-1/2}$, the adiabatic one, and furthermore it gives rise to a third pole due to heat conduction. The latter has, however, much smaller weight:

$$\frac{I_{\text{heat cond.}}}{I_{\text{sound}}} = \frac{\chi_T}{\chi_s} - 1 = R_{\text{LP}} \ll 1, \tag{67}$$

R_{LP} being the Landau–Placzek ratio. In the critical region where $Q \approx 0$, $T \gtrsim T_c$, the situation will change. The phase transition occurring at $T = T_c$ is characterized by [20]

$$\lim_{T \to T_c} \chi_T^{-1}(Q_R) = 0, \tag{68}$$

the critical behavior being

$$\chi_T(Q_R) \propto (T - T_c)^{-\gamma}. \tag{69}$$

Thus inequality (66) is expected to be reversed:

$$\frac{\lambda^2 T}{C_v}\alpha > \chi_T^{-1}. \tag{70}$$

In this case $C(Q_R - Q,\Omega)$ gives rise to a strong central peak in $S(Q_R - Q,\Omega)$ dominating the soft-mode doublet provided that $\langle \Delta \rangle$ is zero, which should be true for T near T_c. Depending on the critical behavior of λ, α, κ, and C_v two cases can be distinguished:

a) $$\frac{\lambda^2 T\alpha^2}{C_v} \gg \left(\frac{Q^2\kappa}{C_v} + \left\langle \frac{\gamma}{2\omega} \right\rangle\right)^2. \tag{71}$$

This situation has been considered by Schneider [6]. There are two weak soft-mode resonances with frequencies

$$\Omega_s(Q_R - Q) \approx \pm\lambda \sqrt{\frac{T}{C_v}}\,\alpha(Q_R - Q) \tag{72}$$

which may remain finite at $T = T_c$, and a strong central peak. Because of equations (68) to (72) its width

$$\Gamma_{Q_R - Q} = \left(\frac{Q^2\kappa}{C_v} + \left\langle\frac{\gamma}{2\omega}\right\rangle\right) \cdot \frac{C_v}{\chi_T(Q_R - Q)\,\lambda^2\,T\alpha^2(Q_R - Q)} \tag{73}$$

vanishes with the critical behavior

$$\Gamma_{Q_R - Q} \propto (T - T_c)^{\gamma}, \tag{74}$$

whereas its height $S(Q_R - Q, \Omega = 0)$ diverges as $(T - T_c)^{-2\gamma}$. These results agree with those in Ref. [6].

b) $$\frac{\lambda^2\,T\alpha^2}{C_v} \ll \left(\frac{Q^2\kappa}{C_v} + \left\langle\frac{\gamma}{2\omega}\right\rangle\right)^2. \tag{75}$$

Here the two soft-mode poles have disappeared in favor of one strong central peak.

The recent detailed experimental results [3] indicate that $SrTiO_3$ can be classified under case a), whereas for $KMnF_3$ relation (75) seems to be fulfilled.

It is impossible to draw conclusions concerning the detailed Q-dependence of $S(Q_R - Q, \Omega)$ since the behavior of α is not determined. If the anharmonic coupling parameters approximated by (49) and (50) vary continuously at $T = T_c$, α should vanish for $Q \to 0$:

$$\alpha(Q_R - Q) = Q + Q(Q^2), \tag{76}$$

for in the ordered phase Q_R is equivalent to the center of the Brillouin zone. For the same reason $\gamma(Q)$ and $\Delta(Q)$, being the difference of quantities which become equivalent at $T = T_c$ [see equations (27) and (28)], will go to zero for $T \to T_c$. Under these circumstances the structure factor $S(Q_R - Q, \Omega)$ has, for $T \approx T_c$, exactly the hydrodynamic form (21), even in its Q dependence.

Summary

Starting from a one-mode Hamiltonian describing the soft mode we have derived an expression for the structure factor $S(\vec{k}, \Omega)$ which can account for the neutron-scattering data for $SrTiO_3$ and $KMnF_3$ near the transition temperature. The same mathematical analysis which has to be performed for $\vec{k} \approx \vec{0}$ to deal with the hydrodynamic singularities is applied to the case $\vec{k} \approx \vec{Q}_R$. This is necessary since the symmetry of the dispersion curve of the soft mode in these two substances [16, 17] leads to hydrodynamic singularities in the phonon self-energy for $\vec{k} \approx \vec{Q}_R$. The resulting expression for the structure factor has the same form as in the more phenomenological theories and comprises the result found by Enz [9]. In the framework of this model it is difficult to draw conclusions about the quantitative behavior of the parameters entering $S(\vec{k}, \Omega)$.

We should like to stress again the fact that if we applied our calculations to an evaluation of $S(\vec{k},\Omega)$ for $\vec{k} \approx \vec{0}$ rather than $\vec{Q}_R$, no assumptions on the phonon spectrum would be necessary. The treatment of the hydrodynamic singularities discussed in Section III is inevitable in this case and our formulae therefore also give a microscopic foundation to the explanation of the central peak in Nb_3Sn by Shirane and Axe [4].

The assumption of the approximate symmetry of the dispersion curve is difficult to test in a quantitative manner and is special for $SrTiO_3$ and $KMnF_3$. On the other hand, it has the direct consequence that the structure factor for wave vectors near Q_R exhibits a behavior which differs from that of other vectors in the Brillouin zone. Other mechanisms of phonon collisions which single out the R corner are not conceivable. Microscopic explanations involving four-phonon processes lead to a form for $S(\vec{k},\Omega)$ continuously varying over the whole zone. In contrast, the approximate symmetry assumed here accounts for the special form at the R corner.

Acknowledgments

We should like to express our gratitude to T. Schneider for his help and interest and for several valuable discussions. We also thank C. P. Enz for providing us with results prior to publication and for discussions, and K. A. Müller for careful reading of the manuscript. One of us (H.B.) thanks the Swiss National Foundation for financial support.

APPENDIX

Using (13) and a similar definition for F, (18) and (19) are transformed into

$$\sigma_F(k, z_\nu) = \frac{i}{2} \sum_{k_1 k_2} V_3(-k, k_1, -k_2) \frac{1}{-i\beta} \sum_{z_\alpha} F(k_1, k_2, k; z_\alpha, z_\nu - z_\alpha) \tag{A1}$$

and

$$\begin{aligned} F(k_1, k_2, k_3; z_\nu, z_\mu) = G(k_1, z_\nu)\, G(k_2, -z_\mu) \Bigg[& V_3(-k_1, k_2, k_3) + \frac{i}{2} \sum_{k'k''} V_4(-k_1, k_2, k', -k'') \\ & \times \frac{1}{-i\beta} \sum_{z_\alpha} F(k', k'', k_3; z_\alpha, z_\nu + z_\mu - z_\alpha) \\ & + i \sum_{k'k''k'''} V_3(-k_1, k', k'')\, V_3(-k'', -k''', k_2) \\ & \times \frac{1}{-i\beta} \sum_{z_\alpha} G(k'', z_\nu - z_\alpha)\, F(k', k''', k_3; z_\alpha, z_\nu + z_\mu - z_\alpha) \Bigg]. \end{aligned} \tag{A2}$$

The sums over z_α are evaluated by means of the equality

$$\frac{1}{-i\beta} \sum_{z_\alpha} f(z_\alpha) = \oint_C \frac{dz}{2\pi} N_0(z) f(z) \tag{A3}$$

with

$$N_0(z) = \frac{1}{e^{\beta z} - 1}. \tag{A4}$$

The contour c, which is described in Refs. [11], [12] and [14], leads along the branch-lines of $f(z)$. These are

$$\operatorname{Im} z = 0 \quad \text{for} \quad G(k, z)$$

as well as

$$\operatorname{Im} z = 0$$

and

$$\operatorname{Im} z' = 0 \quad \text{for} \quad F(\ldots; z, z').$$

Taking the limit $z_\nu \to \Omega + i\delta$ as required in (14) this procedure leads to (22) and (23).

REFERENCES

[1] K. A. MUELLER, E. BRUN, B. DERIGHETTI, J. E. DRUMHELLER and F. WALDNER, Phys. Letters *9*, 223 (1964); K. A. MUELLER, W. BERLINGER and F. WALDNER, Phys. Rev. Letters *21*, 814 (1968); *26*, 13 (1971).
[2] E. PYTTE and J. FEDER, Phys. Rev. *187*, 1077 (1969); *B1*, 924, 4803 (1970).
[3] S. M. SHAPIRO, J. D. AXE, G. SHIRANE and T. RISTE, preprint; T. RISTE, E. J. SAMUELSEN, K. OTNES and J. FEDER, Solid State Commun. *9*, 1455 (1971); and *Structural Phase Transitions and Soft Modes*, edited by E. J. SAMUELSEN (Universitetsforlaget, Oslo, Norway 1971).
[4] G. SHIRANE and J. D. AXE, Phys. Rev. Letters *27*, 1803 (1971).
[5] F. SCHWABL, Phys. Letters *28*, 500 (1972); Z. Physik *254*, 57 (1972).
[6] T. SCHNEIDER, Phys. Rev. *B7*, 201 (1973).
[7] J. FEDER, Solid State Commun. *9*, 2021 (1971).
[8] R. SILBERGLITT, Solid State Commun. *11*, 247 (1972).
[9] C. P. ENZ, Phys. Rev. *B6*, 4695 (1972).
[10] L. P. KADANOFF and P. C. MARTIN, Ann. Phys. (N.Y.) *24*, 419 (1963).
[11] L. J. SHAM, Phys. Rev. *156*, 494 (1967).
[12] H. BECK, Phys. Kondens. Materie *12*, 330 (1971).
[13] W. GOETZE and K. H. MICHEL, Z. Physik *223*, 199 (1969).
[14] L. P. KADANOFF and G. BAYM, *Quantum Statistical Mechanics* (Benjamin, New York 1962).
[15] R. K. WEHNER and R. KLEIN, Physica *52*, 92 (1971).
[16] G. SHIRANE and Y. YAMADA, Phys. Rev. *177*, 858 (1969).
[17] K. GESI, J. D. AXE, G. SHIRANE and A. LINZ, Phys. Rev. *B5*, 1933 (1972).
[18] E. PYTTE, Phys. Rev. Letters *28*, 895 (1972).
[19] K. WEISS, Phys. Kondens. Materie *7*, 201 (1968).
[20] T. SCHNEIDER, G. SRINIVASAN and C. P. ENZ, Phys. Rev. *A5*, 1528 (1972).