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Analysis of anomalous Brillouin scattering in K_2SeO_4

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Abstract. An analysis is presented of the anomalous frequency shift and linewidth of Brillouin scattering in K_2SeO_4 near the normal–incommensurate phase transition at $T_i = 130$ K. Fluctuations are included up to second order, which allows incorporation of the regime above T_i. Below T_i, terms to second order in the fluctuations and a bilinear part in the order parameter and the fluctuations each contribute significantly to the anomalies. Results for relaxation times and coupling parameters are compared with findings from other sources.

This paper is concerned with an analysis of the acoustic anomalies associated with the normal–incommensurate transition in K_2SeO_4 ($T_i = 130$ K). The analysis adds to previous ones (Cho and Yagi 1981, Hauret and Benoit 1982, Luspin *et al* 1984) in that both Brillouin shift and damping are treated up to *second* order in the order-parameter fluctuations. As it appears, this leads to a consistent and quantitative account of the elastic behaviour at *either* side of the transition with realistic values of the parameters. The anomalies at T_i of the velocity and damping of acoustic waves in K_2SeO_4 have been measured, in particular for the C_{11} longitudinal mode (crystal axes chosen such that $b > c > a$), by a number of authors with Brillouin scattering (Yagi *et al* 1979, Rehwald *et al* 1980, Cho and Yagi 1981, Hauret and Benoit 1982, Luspin *et al* 1984, Benoit *et al* 1985) and ultrasonic techniques (Rehwald *et al* 1980, Hoshizaki *et al* 1980). In the present work we will mainly rely on the high-quality Brillouin data collected by Hauret and Benoit (1982).

Theoretical treatments of acoustic anomalies invoked by softening phonon modes (Yao *et al* 1981, Horikx *et al* 1989) are usually formulated in terms of the equations of motion of, on the one hand, the acoustic strains e_i and the soft-phonon coordinate Q on the other. The former are observed with Brillouin scattering at a wavevector near the centre of the Brillouin zone, and the latter is in the present case to be associated with the incommensurate wave at wavevector $\boldsymbol{q}_i$. The strains develop anomalies by a coupling to the soft phonons, which by symmetry arguments is (to lowest order) of the form eQ^2 (Rehwald *et al* 1980, Yao *et al* 1981). Below T_i, Q acquires a non-zero average $\langle Q\rangle$ in addition to a fluctuating part δQ, i.e.

$$Q(\boldsymbol{q}) = \langle Q\rangle\delta(\boldsymbol{q} - \boldsymbol{q}_i) + \delta Q(\boldsymbol{q}). \tag{1}$$

Accordingly, two contributions to the coupling may be distinguished. One is proportional to $e\langle Q\rangle\delta Q$, i.e., bilinear in e and δQ, while the other goes as $e\delta Q^2$ (Yao *et al* 1981, Luspin *et al* 1982, Luspin *et al* 1984). Because phase fluctuations are decoupled from the strains in the case of a coupling of the form eQ^2 (Horikx *et al* 1989), δQ here is to be associated with the amplitudons. Above T_i, $e\langle Q\rangle\delta Q$ vanishes, but the fluctuating second-order part $e\delta Q^2$ remains. From the analysis of Brillouin scattering in K_2SeO_4 below, it appears that below T_i the parts $e\langle Q\rangle\delta Q$ and $e\delta Q^2$ are of comparable magnitudes. Further evidence is found for a gap in the dispersion near $\boldsymbol{q}_i$ at the phase transition.

The equations of motion of the coupled strain and soft modes have already been worked out to second order in δQ in a previous paper (Horikx *et al* 1989). Use was essentially made of the Langrange formalism in a classical continuum approximation, and the coupling was represented by the energy density

$$\sum_{i=1}^{3} g_i e_i QQ^* + \left(\sum_{i,j=1}^{3} h_{ij} e_i e_j + \sum_{i=4}^{6} h_{ii} e_i^2\right) QQ^* \tag{2}$$

such as is appropriate for β-K_2SO_4-type crystals, with g_i and h_{ij} being the coupling coefficients. For C_{11}-mode acoustic phonons, the coupling was found to affect the Brillouin frequency ν and the linewidth Δ according to

$$\nu = \nu_0 + (k_1^2 h_{11} \rho_0^2 / 2\pi\omega\rho_m) - K_1/(1+\omega^2\tau^2) - K_2\{\tfrac{1}{2}[(1+\tfrac{1}{4}\omega^2\tau^2)^{1/2} - 1]\}^{1/2}/(\omega\tau)^{1/2} \tag{3a}$$

$$\Delta = \Delta_0 + K_1(2\omega\tau)/(1+\omega^2\tau^2) + K_2[\![\{2[(1+\tfrac{1}{4}\omega^2\tau^2)^{1/2} + 1]\}^{1/2} - 2]\!]/(\omega\tau)^{1/2}. \tag{3b}$$

Here,

$$K_1 = k_1^2 g_1^2 \rho_0^2 / \pi\mu\rho_m \omega \Omega_a^2(0) \tag{4a}$$

$$K_2 = k_1^2 g_1^2 k_B T / 16\pi^2 \rho_m (\mu\Gamma D_1 D_2 D_3 \omega^3)^{1/2} \tag{4b}$$

in which ν_0 and Δ_0 are the non-anomalous parts of ν and Δ, ω is the unperturbed angular frequency of the acoustic phonons, k_1 is the modulus of their wavevector, ρ_m is the mass density, and $\rho_0^2 = \langle Q\rangle\langle Q^*\rangle$. The quantities μ, $\Omega_a(0)$, Γ, and $\tau = \Gamma/\Omega_a^2(0)$ respectively denote the effective mass density, the $q = 0$ angular frequency, the damping, and the relaxation time of the amplitudons. The parameters D_1, D_2, and D_3 refer to the amplitudon dispersion relation, which is assumed to read $\Omega_a^2(\boldsymbol{q}) = \Omega_a^2(0) + \Sigma_i D_i q_i^2/\mu$. The second term in equation (3*a*) derives directly from a contribution of the form $he^2\rho_0^2$ to the elastic energy. The terms with K_1 in equations (3*a*) and (3*b*) are due to the effective bilinear coupling $e\langle Q\rangle\delta Q$ between the amplitudon and the strains. The terms with K_2, i.e., the fluctuation terms, result from the $e\delta Q^2$ part of the coupling. Above T_i, the $e\delta Q^2$ part is the lowest-order interaction accounting for the frequency and linewidth anomalies. In this regime, equations (3*a*) and (3*b*) remain valid provided ρ_0 and K_1 are set to zero, and the parameters are interpreted as to pertain to the high-temperature soft mode instead of the amplitudon. In equations (4*a*) and (4*b*) minor corrections to K_1 and K_2 resulting from the second term in equation (2) are ignored.

Equations (3*a*) and (3*b*) have been least-squares adjusted to the Brillouin data collected by Hauret and Benoit (1982) for the C_{11} elastic constant, following conversion of these data to frequencies. In the fits, Δ_0 is set equal to zero and ν_0 is assumed to be independent of the temperature, as is suggested by Brillouin results extending over a much wider range of temperatures (Rehwald *et al* 1980). Further, the relaxation time is assumed to vary with the temperature according to

$$1/\tau(T) = (1/\tau_{a,s}^*)(|T - T_i|/T_i) + 1/\tau_0 \tag{5}$$

where the subscripts a and s refer to the amplitudons ($T < T_i$) and high-temperature soft

Table 1. Output values of the fit to the C_{11}-mode Brillouin frequency and linewidth in K_2SeO_4.

τ_a^* (10^{-14} s)	τ_s^* (10^{-14} s)	τ_0 (10^{-11} s)	T_i (K)	R (GHz)	$K_2(T_i)/K_{1,\infty}$	$K_{1,\infty}$ (GHz)
2.03 ± 0.13	7.3 ± 1.4	3.4 ± 0.7	129.9 ± 0.1	5.5 ± 0.6	1.83 ± 0.13	2.2 ± 0.1

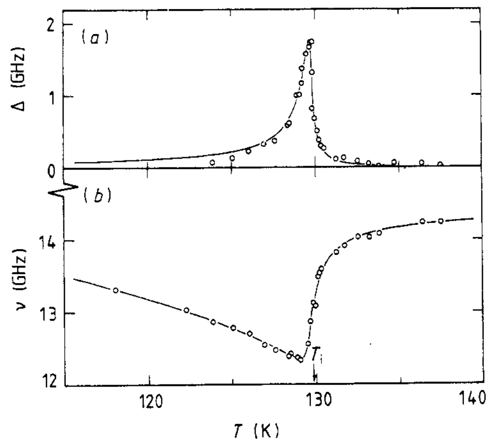

Figure 1. Temperature dependences of (a) the Brillouin frequency ν, and (b) the linewidth Δ (FWHM) of C_{11}-mode longitudinal acoustic phonons in K_2SeO_4. The data, pertaining to a 90° scattering geometry and an incident laser wavelength of 514.5 nm, are from Hauret and Benoit (1982) after conversion of the elastic constants back to frequencies. Curves are best fits of equations (3a) and (3b) with equations (5) and (6) inserted. Above T_i, only the fluctuation part contributes to the anomaly.

phonons ($T > T_i$), respectively. The rate $1/\tau_0$ has been added to the usual $|T - T_i|$-dependent relaxation rate to express that a gap in the soft-mode and amplitudon dispersion prevents $1/\tau$ from reaching zero at the phase transition. A gap further renders K_1 temperature dependent in a narrow range of temperatures around T_i, where ρ_0 vanishes, but $\Omega_a(0)$ remains finite. Further out from the transition, $\rho_0/\Omega_a(0)$ is known to assume a more-or-less constant value (Petzelt 1981). To accommodate the associated variations in K_1, we adopt in a heuristic way

$$K_1(T) = K_{1,\infty}(1 - \tau/\tau_0) \tag{6}$$

where $K_{1,\infty}$ is the value of K_1 at some distance from T_1. In the second term of equation (3a), it is satisfactory to let ρ_0^2 below T_i scale with $(T_i - T)^{0.70}$, i.e., $k_1^2 h_{11}\rho_0^2/2\pi\omega\rho_m = R[(T_i - T)/T_i]^{0.70}$. This represents a simple but adequate empirical parametrisation of the temperature dependence of the order parameter in the incommensurate phase (Horikx *et al* 1988), such as previously found in K_2SeO_4 from the elastic behaviour (Hauret and Benoit 1982). In summing up, apart from ν_0 the fitting parameters are T_i, τ_a^*, τ_s^*, τ_0, and R, and finally the prefactors of the bilinear and the fluctuation terms, or rather $K_{1,\infty}$ and $K_2(T_i)/K_{1,\infty}$.

The results of the simultaneous least-squares adjustment of these parameters to the frequency and linewidth are collected in table 1. In figure 1, where equations (3a) and (3b) with the fitted parameters inserted are compared with the data, it is seen that the theory faithfully reproduces the anomalous parts of the frequency and linewidth. As regards the gap, it should be pointed out that the fit markedly deteriorates when τ_0^{-1} is set equal to zero, although, as is seen from τ_0 and $\tau_{a,s}^*$ in conjunction with equation (5), the effects of the gap do not become appreciable until a few tenths of degrees from the transition.

It is of interest to compare the output values of the fit with findings from the literature. As for the parameters which model the behaviour of τ, we first consider τ_a^*. From the Brillouin linewidth Hauret and Benoit (1982), ignoring the fluctuation term $e\delta Q^2$, found $T_i\tau_a^* = 2.6 \times 10^{-12}$ s K, or $\tau_a^* = 2.0 \times 10^{-14}$ s. In a similar way, Luspin *et al* (1984) found $T_i\tau_a^* = 2.85 \times 10^{-12}$ s K, or $\tau_a^* = 2.2 \times 10^{-14}$ s, from the linewidths in three different scattering geometries. Both values concur remarkably with the result of the present analysis, which does include the fluctuation part. Furthermore, τ_a^* may be estimated from Raman scattering, in particular from the high-quality data by Unruh *et al* (1979). Plotting the ratio Ω^2/Γ versus the temperature in the interval from $T_i - 20$ K to $T_i - 4$ K, we find a straight line with a slope of $2\pi \times 3$ cm^{-1} K^{-1}, yielding $\tau_a^* = 1.4 \times 10^{-14}$ s. This finding is not far from the present fitted value, which is mainly based on the data between $T_i - 2$ K and T_i. As for the relaxation of the soft mode above the transition, this mode is Raman inactive, but some of its properties may be deduced from neutron-scattering data. Iizumi *et al* (1977) measured the development of the soft-mode energy with temperature, to find that from T_i up to $T_i + 30$ K the squared energy varies approximately with 0.05 meV^2 K^{-1}, while at 15 K above T_i the energy profile is about 1 meV wide. From these results, we assess $\tau_s^* \sim 10^{-13}$ s, within the uncertainties in accord with the present value.

The present result for τ_0, when combined with the amplitudon damping in the relation $\tau = \Gamma/\Omega_a^2(0)$, allows estimation of the gap in the dispersion remaining at the transition. From Raman scattering (Unruh *et al* 1979) the amplitudon width Γ is found to be $2\pi \times 20$ cm^{-1} at 4 K below T_i, which combined with the present τ_0 yields a gap of 1.8 cm^{-1}. From neutron scattering, Iizumi *et al* (1977) have deduced 0.17 meV, or 1.4 cm^{-1}, for the soft-mode gap at 130 K. Because the phason, amplitudon, and soft-mode dispersions presumably coincide at the transition, and because the phason gap of incommensurate systems is nearly independent of temperature (Blinc *et al* 1980, Zumer and Blinc 1981, Rutar *et al* 1982, Blinc *et al* 1985, 1986), the present result may further be compared with determinations of the phason gap. The data of Quilichini and Currat (1983) indicate that this gap is about 3.5 cm^{-1} at 8 K below T_i, which, within the uncertainties, is in accord with our results.

We next turn to an estimate of the parameter $K_{1,\infty}$. We use $\rho_m = 3.05 \times 10^3$ kg m^{-3}, $k_1 = 2.66 \times 10^7$ m^{-1}, and $\omega = 8.8 \times 10^{10}$ s^{-1}. Concerning the asymptotic value of the quantity $\rho_0/\Omega_a(0)$ occurring in $K_{1,\infty}$, we note that from an x-ray structural study (Yamada and Ikeda 1984) the SeO_4 tetrahedra were found rotated by 7.5 deg at 113 K, which corresponds to $\rho_0 \approx 1.5 \times 10^{-11}$ m. At this temperature, the amplitudon frequency is found to be 21 cm^{-1} from Raman experiments (Unruh *et al* 1979, Fleury *et al* 1982, Massa *et al* 1982), leading to $\rho_0/\Omega_a(0) \approx 3.8 \times 10^{-24}$ ms. The quantity g_1 may be derived from thermal expansion data via the relation $g_i = -(\Sigma_j C_{ij}\delta\alpha_j)/(\mathrm{d}\rho_0^2/\mathrm{d}T)$ evaluated at T_i, where C_{ij} are the elastic constants and $\delta\alpha_j$ are the anomalous parts of the thermal expansion coefficients. The quantity $\mathrm{d}\rho_0^2/\mathrm{d}T$ is in turn obtained from the temperature dependence of the normalised order parameter (Kudo and Ikeda 1981) combined with ρ_0 at 113 K given above, to yield $\mathrm{d}\rho_0^2/\mathrm{d}T \approx -2.5 \times 10^{-23}$ m^2 K^{-1}. Inserting further C_{ij} (Hauret and Benoit 1982) and $\delta\alpha_{ij}$ (Iskornev and Flërov 1983), we then find $g_1 \approx -2 \times 10^{29}$ kg s^{-2}. The effective mass μ of the amplitude mode may be determined from the observed variation of the amplitudon frequency with a uniaxial stress σ_1 applied along the *a* axis. Experimentally, Wada *et al* (1982) found $\mathrm{d}\Omega_a^2/\mathrm{d}\sigma_1 = -400$ cm^{-2} kbar^{-1}, or -1.4×10^{17} Pa^{-1} s^{-2}, at 22 K below T_i. From Landau theory, one has the relation $\mathrm{d}\Omega_a^2/\mathrm{d}\sigma_1 = 4g_1/\mu C_{11}$ (Wada *et al* 1982, Horikx *et al* 1989), from which we deduce $\mu \approx 0.14 \times 10^3$ kg m^{-3}, or approximately $0.05\rho_m$. Inserting the above result into equation

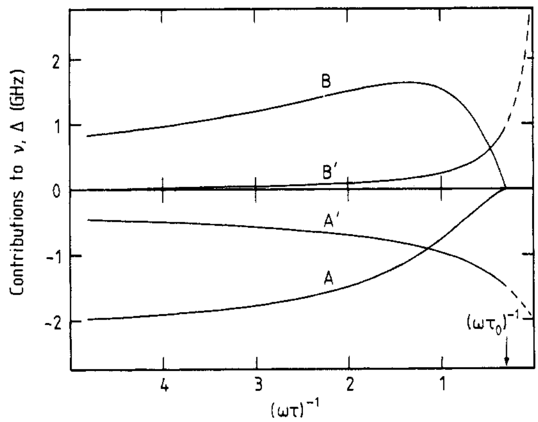

Figure 2. Contributions to the Brillouin frequency ν (curves A, A'), and linewidth Δ (curves B, B') below T_i versus $(\omega\tau)^{-1}$, as derived from the fits of figure 1: curves A, B, bilinear part; curves A', B', fluctuation part. Relaxation time τ is limited to τ_0 by the gap at T_i; $\omega = 8.8 \times 10^{10}\,s^{-1}$. Not shown is the contribution of the second term in equation (3*a*), which amounts to $+0.16$ GHz at $(\omega\tau)^{-1} = 4$, decreasing to zero at T_i.

(4*a*), we finally arrive at the estimate $K_{1,\infty} \sim 3.5$ GHz, which is in accord with the result from the fit within the uncertainties.

To conclude the comparison with estimates from other sources, we consider $K_2(T_i)/K_{1,\infty}$, which represents the magnitude of the fluctuation term relative to the bilinear term. Given μ, ω, Γ, and the asymptotic value of $\rho_0/\Omega_a(0)$ already discussed, only the ratio $(D_1D_2D_3)^{1/3}/\mu$ remains to be estimated. D_2/μ and D_3/μ may be obtained from the neutron scattering data collected by Iizumi *et al* (1977) for the soft-mode dispersion at 130 K. They found $\partial(\hbar\omega)^2/\partial k_2^2 = 570\,\text{meV}^2\,\text{Å}^2$ and $\partial(\hbar\omega)^2/\partial k_3^2 = 110\,\text{meV}^2\,\text{Å}^2$, leading to $D_2/\mu = 13 \times 10^6\,m^2\,s^{-2}$ and $D_3/\mu = 2.5 \times 10^6\,m^2\,s^{-2}$. No data are available to estimate D_1, but in consideration of the fact that the structure of K_2SeO_4 derives from a hexagonal parent structure (Shiozaki *et al* 1977, Unruh 1981, *Ann. Rep. Res. React. Inst. Kyoto. Univ.* 1984), we assume $D_1 \approx D_2$. We thus find $(D_1D_2D_3)^{1/3}/\mu \approx 7.5 \times 10^6\,m^2\,s^{-2}$, which, when inserted together with the parameters already estimated above, yields $K_2(T_i)/K_{1,\infty} \sim 1.5$, again in agreement with the result from the fit. Finally, it is of interest to examine to what extent the gap affects the bilinear and fluctuation parts of the Brillouin frequency and linewidth below T_1. Figure 2 shows these contributions as a function of $(\omega\tau)^{-1}$, as recalculated from the K_1 and K_2 parts of equations (3*a*) and (3*b*) with the fitted parameters inserted. The magnitudes of the fluctuation parts are seen to increase monotonically with decreasing τ^{-1}. Accordingly the gap, which limits these terms to their value at $(\omega\tau_0)^{-1}$, smoothes the anomaly to a substantial degree. This is especially the case for the linewidth, which has the strongest τ^{-1} dependence. In fact, the finite $(\omega\tau_0)^{-1}$ lowers the fluctuation part of the damping by over a factor of four at the transition. The bilinear terms primarily depend on the gap through the associated modification of $\rho_0^2/\Omega_a^2(0)$, resulting, for a gap of the size found, in effects of limited significance at Brillouin frequencies. These conclusions are also arrived at from a best fit of the theory with $(\omega\tau_0)^{-1}$ set to zero, in which the fluctuation part of the linewidth in particular is found to be severely overestimated.

In conclusion, an analysis with inclusion of the coupling quadratic in the order-parameter fluctuations has resulted in a quantitative account of the anomalous Brillouin frequency shift and damping of acoustic phonons both below and above the normal–incommensurate transition in K_2SeO_4. The effects of this coupling are of a magnitude comparable to those of the bilinear coupling. In addition, the dispersion was found to be left with a gap at the transition.

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