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A far-infrared emission study on the phonon self-energy of KCl at high temperature

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Abstract. p-polarised oblique emission spectra of KCl polycrystalline films in the infrared region were measured at temperatures between 40 and 550 °C. Using a method based upon the virtual-mode theory of thin films, they are analysed by introducing an empirical form for the phonon self-energy in a dielectric response function. The damping function $\Gamma(\omega)$—the imaginary part of the self-energy—obtained by a least-squares fit for the observed spectra takes small values near the transverse optic (TO) mode frequency but peaks strongly around the longitudinal optic (LO) mode frequency, and has fine structure at low temperature. The maximum value of $\Gamma(\omega)$ is about 50 cm^{-1} around the LO mode frequency, almost independently of temperature. The lineshape of $\Gamma(\omega)$ becomes considerably broader, however, at high temperatures. We found that the magnitude of $\Gamma(\omega)$ obtained experimentally shows a linear temperature dependence. The quasi-harmonic TO and LO mode frequencies and dampings near these frequencies are also estimated and their temperature dependences are discussed.

1. Introduction

A family of alkali halides and related materials has aroused considerable interest within the study of lattice phonon anharmonicity, because of their simple crystal structure. The phonon–phonon interaction represented by a complex self-energy in a dielectric response function makes their effective mode frequencies and dampings dependent on frequency and temperature (Cowley 1963).

For KCl, anharmonic effects on the $q \simeq 0$ transverse optic (TO) mode frequency and damping have been investigated by Lowndes and Rastogi (1976) at temperatures between 2 and 300 K and under hydrostatic pressures of 0–7 kbar. The frequency-dependent real and imaginary parts of the $q \simeq 0$ self-energy arising from the cubic lattice anharmonicity have been calculated at 300 K from the complex refractive index measured by asymmetric Fourier transform spectroscopy (Johnson and Bell 1969). Anharmonic effects reflecting the fine structure of the self-energy have been observed in the hyper-Raman spectra as an anomalous response near the longitudinal optic (LO) phonon frequencies (Vogt and Presting 1985). Such anharmonic effects on the lattice become large at high temperatures.

In this paper we report a high-temperature study of phonon anharmonicity for KCl made using the far-infrared emission technique. The observed spectra are analysed using an empirical form of the self-energy. An infrared emissivity measurement of the thin

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metal-backed films for oblique emission angles enables us to investigate the self-energy over a wide frequency range around the restrahlen band frequency. As discussed previously (Hisano *et al* 1972, 1973), this technique provides considerably more information than conventional infrared experiments with bulk samples.

2. Experimental details

KCl polycrystalline films were evaporated onto platinum plates heated at 120 °C in a vacuum of 7×10^{-3} Pa. Samples having dimensions of 30×30 mm^2 with thicknesses from 2 to 3 μm were prepared. This range of thickness, an emission angle of 45° and p polarisation were found to be suitable for KCl for obtaining information associated with both the TO and LO modes. Far-infrared emission spectra have been measured using a FTIR spectrometer with a Mylar beam splitter 6 μm thick and with a Golay cell detector (Hisano and Tanaka 1988). The whole optical system was enclosed in a housing with a dry nitrogen gas atmosphere to prevent oxidation of the sample and infrared absorption by vapour in the air. To reduce the background, the sample housing, with a radiation shield, was cooled by circulating water in a similar way to that employed previously (Hisano 1981). The entrance optics were designed in such a way that the parallel flux of radiation from the sample/black body was collected into the interferometer. The resolution of the spectral measurement in the present study was 3.2 cm^{-1} after apodisation through the Hamming window.

Measurements of the spectra were performed at elevated temperatures up to 550 °C. The temperature dependence of the spectra for the sample that was 2.6 μm thick is shown in figure 1, where the experimental data (full circles) are normalised with the black-body radiation intensity. The lower limit for the temperature where a reliable spectrum was obtained for analysis was about 41 °C in the present study. Spectra observed for film 2.1 μm thick have been given elsewhere (Tanaka and Hisano 1988). These spectra show similar temperature dependences. The spectra observed at low temperature show a single peak near 135 cm^{-1} and anomalously broad double peaks near 210 cm^{-1} with fine structures. The former is located near the TO mode frequency and the latter near the LO mode. These peaks become broad and show complex lineshapes at elevated temperatures.

3. Infrared response and spectral analysis

According to the virtual-mode theory proposed by Kliewer and Fuchs (1966), the infrared response for an ionic film of thickness a observed at the emission angle θ and for p polarisation is characterised by the following equation:

$$L_1 = 1 - (i\beta/\beta_0\varepsilon(\omega)) \tan \beta a \tag{1}$$

where $\beta = 2\pi\omega(\varepsilon(\omega) - \sin^2\theta)^{1/2}$, $\beta_0 = 2\pi\omega \cos\theta$ and $\varepsilon(\omega)$ is the dielectric function for frequency ω. The emissivity $E(\omega)$ for the metal-backed thin film is written, using equation (1) and $P_1 = (2 - L_1)/L_1$, as

$$E(\omega) = 1 - |P_1|^2. \tag{2}$$

For the long-wavelength optic phonon, results of the anharmonic lattice theory using thermodynamic Green function techniques (Cowley 1963) lead to a response function

$$G^{-1}(\omega) = \omega_0^2 - \omega^2 + 2\omega_0(\Delta(\omega) - i\Gamma(\omega)) \tag{3}$$

where ω_0 is the harmonic frequency. $\Delta(\omega)$ and $\Gamma(\omega)$ are the shift and the damping of

the self-energy caused by anharmonic interaction. The effective phonon frequency of the anharmonic phonon is represented as

$$\tilde{\omega}_0^2 = \omega_0^2 + 2\omega_0\Delta(\omega). \tag{4}$$

According to perturbation theory for a many-body system, the lowest-order contribution to the shift function can be written as

$$\Delta(\omega) = \Delta_0 + \Delta_1 + \Delta_2(\omega) \tag{5}$$

where Δ_0 represents thermal expansion. Δ_1 arises in the first order and frequency-dependent $\Delta_2(\omega)$ arises in the second order (cubic contribution). $\Gamma(\omega)$, which arises in the second order, reflects the two-phonon density of states. The shape of the two-phonon density of states generally shows two peaks related to the sum and the difference processes. The former is located near the LO mode frequency and the latter below the TO mode frequency.

The infrared response for the weak anharmonic lattice may be given by a frequency-dependent dielectric constant

$$\frac{\varepsilon(\omega)}{\varepsilon_\infty} = \frac{\omega_L^2 - \omega^2 + 2\omega_T(\Delta_2(\omega) - i\Gamma(\omega))}{\omega_T^2 - \omega^2 + 2\omega_T(\Delta_2(\omega) - i\Gamma(\omega))} \tag{6}$$

where ω_L and ω_T are, respectively, the quasi-harmonic LO and TO frequencies including Δ_0 and Δ_1 for the TO mode. Equation (6) would give the renormalised LST relation for $\omega = 0$.

A spectral lineshape analysis has been made in a similar way to that employed previously (Hisano and Tanaka 1986). The effective mode frequencies estimated from the observed spectra are of the renormalised quasi-harmonic frequencies $\tilde{\omega}_T$ and $\tilde{\omega}_L$. These are

$$\tilde{\omega}_T^2 = \omega_T^2 + 2\omega_T\Delta_2(\tilde{\omega}_T) \tag{7}$$

$$\tilde{\omega}_L^2 = \omega_L^2 + 2\omega_T\Delta_2(\tilde{\omega}_L). \tag{8}$$

Since the theoretical lineshape of the high-temperature self-energy for KCl is not available, we have introduced an empirical form for the self-energy in the dielectric response function as follows:

$$\Delta_2(\omega) - i\Gamma(\omega) = \sum_{j=1}^{5} \frac{\omega_j^2\rho_j}{\omega^2 - \omega_j^2 + i\omega\gamma_j}. \tag{9}$$

We expect that one Lorentzian will represent the contribution from the two-phonon difference processes and the others will reflect the two-phonon summation processes, including higher-order contributions. The full curves in figure 1 are the best-fit spectra calculated from the self-energies of equation (9) by adjusting ω_j, γ_j and ρ_j.

In the spectral analysis, however, we have replaced $\Gamma(\omega)$ by an independent parameter Γ_T around the TO mode frequency, because we are not able to estimate both the TO and LO mode dampings using the same functional form. The influence of the two-phonon difference processes on the spectrum is considered to be small near the LO mode frequency. The lineshape fittings have been performed in the ranges 80–160 cm^{-1} and 140–300 cm^{-1} for the TO virtual mode and the LO virtual mode, respectively, where the crossover frequency has been chosen as the minimum point between the virtual TO and LO modes at each temperature. Using a self-energy represented by the two Lorentzians

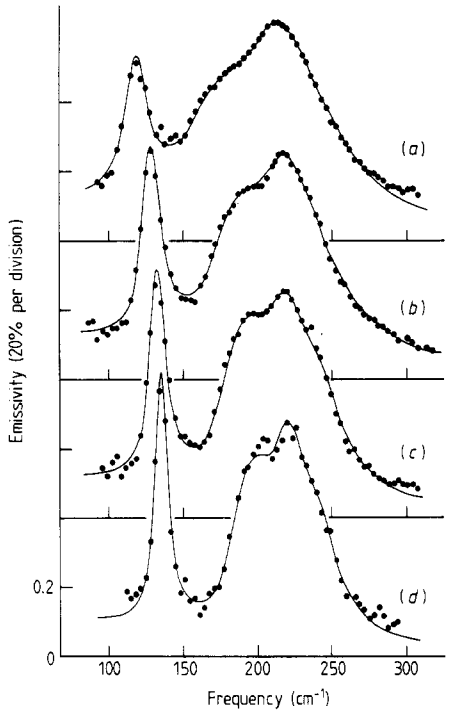

Figure 1. p polarised 45° emission spectra of KCl film of thickness 2.6 μm. Full circles represent experimental data and full curves represent calculated spectra. Temperatures: (*a*) 736 K; (*b*) 513 K; (*c*) 419 K; (*d*) 314 K (41 °C). The data points on the spectrum are plotted with half density for clarity.

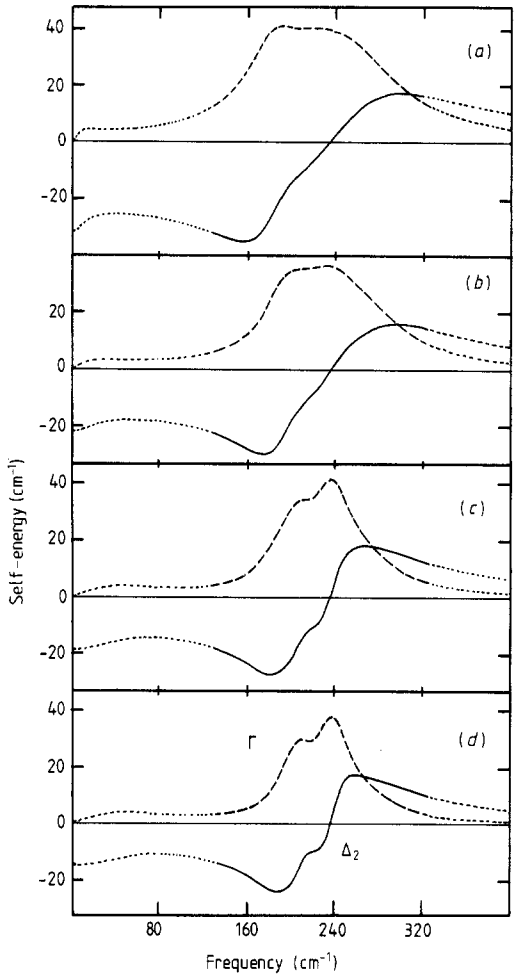

Figure 2. The temperature variation of the empirical form of the self-energy obtained to give a best fit for the spectra in figure 1: full curves, shift (real part); broken curve, damping (imaginary part). Temperatures: (*a*) 736 K; (*b*) 513 K; (*c*) 419 K; (*d*) 314 K (41 °C).

instead of equation (9) was not successful for reproducing the observed spectra, because of the fine structure around the LO mode. This discrepancy becomes large at high temperatures.

4. Discussion

The empirical forms for the self-energies obtained from the lineshape analysis are shown in figure 2. Although the maximum value of the damping function was about 50 cm^{-1} at

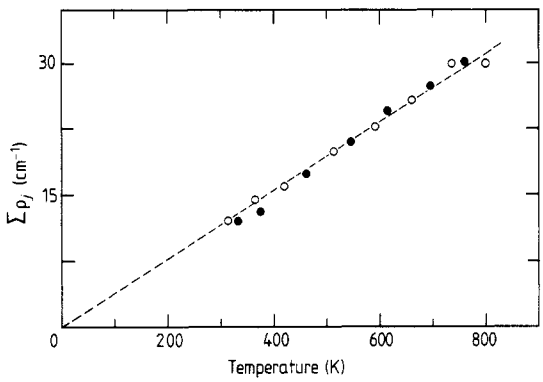

Figure 3. The temperature dependence of a scaling factor of the self-energy function $\Sigma\rho$; ●, 2.1 μm; ○, 2.6 μm.

each temperature, the lineshapes show considerable broadening at elevated temperatures. This indicates that functional forms of the self-energy at high temperatures are not scaled by the form calculated at room temperature. We have estimated the magnitude of the self-energy. In figure 3 we give a plot of the sum of the ρ_j in equation (9), which corresponds to the integrated intensity of $\Gamma(\omega)$ in equation (9) around the restrahlung band, indicating a linear temperature dependence. These results have not been explained by the existing theory. The term for the two-phonon difference processes is omitted in figure 3 because it is located far below the fitting region.

One of the reasons for the broadening of $\Gamma(\omega)$ may be the increase of the quartic contribution to the lowest-order frequency-dependent damping function. The quartic contribution reflects the three-phonon density of states, which has an explicit quadratic temperature dependence. As demonstrated by Eldridge and Staal (1977), three-phonon damping peaks around the TO mode frequency and above the LO mode frequency, where the damping from the two-phonon density of states is small. This contribution is important even at room temperature (Hisano *et al* 1972, Bruce 1973). The large dampings around the LO mode frequency may be accounted for in terms of the lowest-order (cubic) contribution—that is, a two-phonon summation process. This term has an explicit linear temperature dependence at high temperatures because of the Bose–Einstein population factor. However, the temperature dependence of the quasi-harmonic frequency and that of the anharmonic force constant implicitly modify that of the cubic contribution. Consequently the total temperature dependence of this term becomes sub-linear (Bruce 1973). For a similar reason, the quartic term may also be modified, but the temperature dependence of this term will be super-linear at high temperatures. Thus the difference between the temperature dependences for cubic and quartic contributions may cause the broadening of the damping function at high temperatures. The direct phonon–phonon interaction and the interference effect between the one- and two-phonon processes may also produce the spectral change of the damping—in particular, they are large at high frequencies (Bruce 1973, Eldridge and Staal 1977).

In figure 4 we show plots of the renormalised TO and LO mode frequencies estimated in the fitting processes. The former decreases rapidly and the latter slowly at elevated temperatures. These results are accounted for by the signs and absolute values of the shift function at appropriate frequencies in figure 2. Figure 5 shows that the damping function varies with temperature super-linearly near the TO mode and sub-linearly near the LO mode frequencies. This is in good agreement with the theoretical prediction mentioned above; the LO and TO mode dampings are dominated by the cubic and quartic contributions respectively.

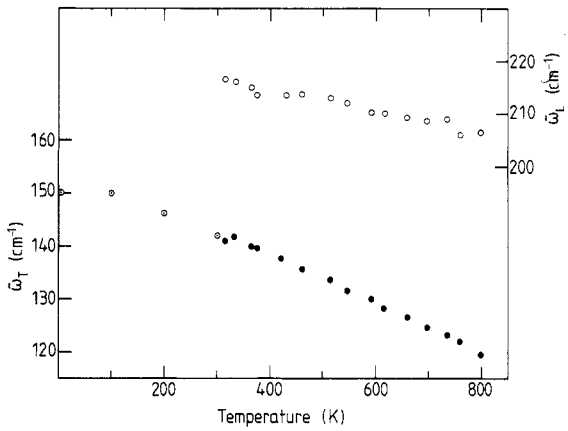

Figure 4. Temperature dependences of the renormalised TO and LO mode frequencies; ●, $\tilde{\omega}_T$; ○, $\tilde{\omega}_L$; ⊙, Lowndes and Rastogi (1976).

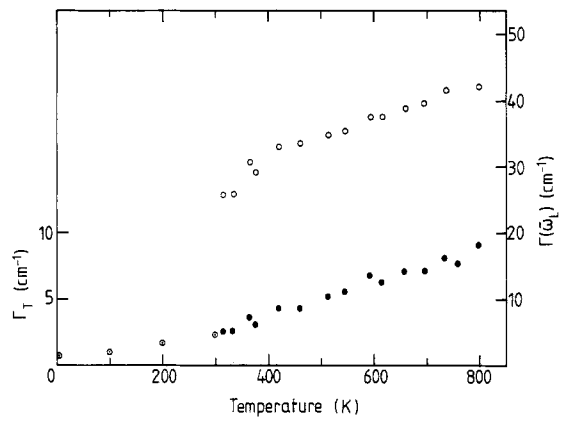

Figure 5. Temperature variations of the damping; ●, Γ_T; ○, $\Gamma(\omega_L)$; ⊙, Lowndes and Rastogi (1976) for the TO mode.

Although differences between the lattice dynamical properties of a polycrystalline film and a single-crystal slab have not been taken into account in the analysis, the results are qualitatively consistent with the existing theory on the phonon anharmonicity for a pure single crystal. The present results for the TO mode with the previous results for low temperatures obtained by Lowndes and Rastogi (1976). The temperature dependences of the renormalised quasi-harmonic frequencies and dampings illustrated in figures 4 and 5 are qualitatively similar to those for KBr and NaCl films (Hisano and Tanaka 1986, 1988). Attempts to fit the spectrum using a self-energy function in which only two-phonon processes are considered have not been successful in the present case, which suggests that higher-order processes or other complex contributions must be taken into account for further quantitative analysis at high temperatures.

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