Temperature dependence of the linewidth of the first-order Raman spectrum for GeO$_2$ powder

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Abstract. The first-order Raman spectrum of A_{1g} mode in GeO$_2$ powder was measured at a temperature range of 130–973 K and the linewidths at these temperatures were obtained. The temperature dependence of the linewidths was analysed by the phonon dispersion curves based on the rigid ion model, and the results show that it was caused perhaps by the cubic anharmonic term in crystal potential energy.

1. Introduction

Studies on the temperature dependence of linewidths and frequencies of normal vibrations of a lattice have been going on for a long time now. Sato (1983) has done experimental investigations and the other workers have investigated ZnSe and ZnTe (LaCombe and Irwin 1970), cuprous halides (Fukumoto *et al* 1976), 3C-type SiC (Olego and Cardona 1982) with zinc blende structure, and also for some materials (Menendez and Cardona 1984) with diamond structure. For more complex crystal structures, the lattice mode anharmonicity in NaNO$_2$ has been investigated by Brehat *et al* (1982), in LiNaSO$_4$ and LiKSO$_4$ by Teeters and Frech (1982), its Raman study of anharmonic effects in –LiIO$_3$ by Cerdeira *et al* (1983), and KTa$_{1-x}$Nb$_x$O$_3$($x = 0.018$) by Rytz *et al* (1983), and LaF$_3$ by Liarokapis *et al* (1985). All these studies discuss the temperature dependence of linewidth and frequency of the cubic and quartic anharmonic terms of the crystal potential energy.

On the other hand, the theoretical investigations have been performed for alkali halide crystals [Ipatova *et al* (1967), Eldridge and Howard (1973), Lowndes and Rastogi (1976)], and for some crystals with diamond type structure [Dolling and Cowley (1966)]. Theoretical calculations and experiments for some fluorite structure ionic crystals have also been performed [Elliott *et al* (1978), Sato and Tateyama (1982a, b)]. However, to the best of our understanding, the theoretical calculations of the temperature dependence of the linewidths and frequencies for crystals with more complex structure have not been performed. While experimental investigation has shown that the linewidth of GaSb (Skryabinskii and Ukhanov 1973) with the zinc blende structure is caused only by the cubic anharmonic term, the linewidth of GaP (Bairamov *et al* 1975) with the same structure is caused by the cubic and quartic terms. The same result has been found for crystals like MgO (Jasperse *et al* 1966),

LiF (Heilmann 1958) and NaF (Chang and Mitra 1972) with alkali halide structure. As mentioned earlier (Sato 1983), the frequencies used to analyse the linewidth in many experimental investigations do not relate to the phonon dispersion curves and have almost no physical foundation. The calculations of the linewidths for more complex crystals would be very tedious. Gervais *et al* (1975) investigated the temperature dependence of the linewidth of TO and LOA_2 modes in quartz and reported that the dependence of the linewidth has been interpreted by considering the actual effect of temperature on the one-phonon density of state. Also the linewidth of phonon in TiO_2 was measured by Gervais and Piriou (1974). They showed that the phonon lifetimes in TiO_2 are limited by the cubic anharmonic term.

The infrared spectra for GeO_2 crystal have been measured by Roessler and Albers (1972) and that of Raman spectra by Scott (1970) and Mammone *et al* (1981). More recently the phonon dispersion curves for GeO_2 have been calculated by Gervais and Kress (1985). The temperature dependence of the frequencies for GeO_2 crystal has been investigated by Mammone *et al* (1981) and the relation between the frequencies and the temperatures has been plotted in the figure. But the relation has not been investigated by using the phonon dispersion curves and the quantitative calculations due to the anharmonic theory. Furthermore, the investigation of the linewidths for GeO_2 crystal has not been reported until now. From the above standpoint, the purpose of the present work is to study the temperature dependence of the linewidths for GeO_2 powder, in order to confirm if it can be explained only by the cubic anharmonic term as indicated by Gervais and Piriou (1974) and by the phonon density of state as indicated by Gervais *et al* (1975). In the present work GeO_2 powder has been used as a specimen because of the difficulty in making a single crystal. The linewidths of the powder are different from the crystals in general, but the temperature dependence of the linewidths for GeO_2 powder should be the same as for the crystals. Thus the purpose is achieved by investigating the temperature dependence for GeO_2 powder.

2. Experiment

GeO_2 belongs to the space group D_{4h}^{14}, of which the normal lattice vibration at the Γ point of the Brillouin zone is given on the basis of group theory (Porto *et al* 1967)

$$1A_{1g} + 1A_{2g} + 1A_{2u} + 1B_{2g} + 1B_{2g} + 2B_{1u} + 1E_g + 3E_u.$$

Among these, the active Raman modes are $B_{1g}(\Gamma_3^+)$, $E_g(\Gamma_5^-)$, $A_{1g}(\Gamma_1^+)$ and $B_{2g}(\Gamma_4^+)$, and consequently four first-order Raman spectra are observed. As shown in figure 1, Raman intensities for B_{1g} and E_g modes at room temperature are weak and not apparent and also, one for B_{2g} not so strong and for A_{1g} strong. Thus A_{1g} mode was measured in the present work. The frequency of this mode (700 cm^{-1}) agrees well with the one reported by Mammone *et al* (1981).

The specimen in pellet form of 99-99% purity and 28 ~ 29 μ was made by compressing a white colour powder (Soekawa Chemicals Co.). The Raman spectrum for GeO_2 was measured using a laser Raman spectrophotometer (Nihon Denshi Ul–UV) equipped with a photon counting system. For temperatures above 300 K the specimen was heated in a nichrome furnace, and the temperatures controlled to within $\pm$ 1 K. For
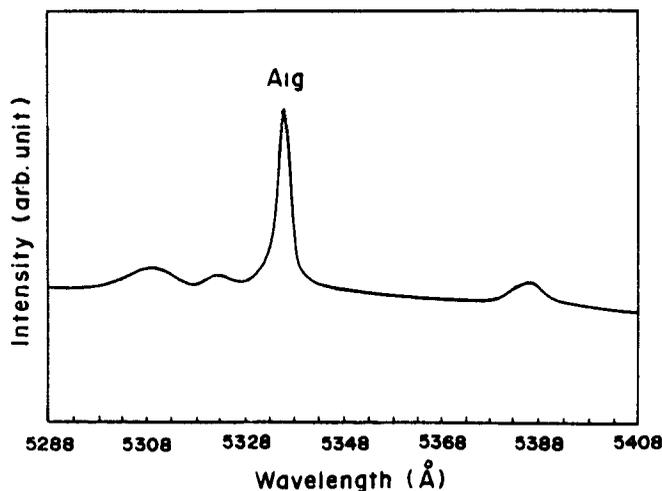
Figure 1. The Raman spectra at 300 K with wavelength (Å).

the measurement at 130 K the temperature of the specimen was determined by the ratio of the intensity of Stokes and anti-Stokes. The beam of an Ar ion laser 5145 Å was used as the light source for Raman excitation. A resolution of about $2 \sim 6\,cm^{-1}$ was used for the measurement. The accuracy of the wavelengths was ± 0.5 Å ($\approx 2\,cm^{-1}$). The Raman frequencies and linewidths were obtained by deconvoluting the recorded spectra using the instrument function.

3. Results and discussion

With increasing temperature the Raman lines for the mode shift to lower frequencies broadened. In order to analyse the temperature dependence of the linewidth, the phonon dispersion curves were calculated with the rigid ion model given by Katiyar and Krishnan (1969). The parameters used to calculate the phonon dispersion are shown in table 1 and the typical dispersion curves in the direction (100), (110) and (001) are shown in figure 2.

The width of the fundamental lattice vibration absorption peak in ionic crystals was calculated by Wallis *et al* (1966) using the Green's function. According to Wallis *et al* (1966), if the Raman linewidth $\Gamma_j(\omega)$ is caused by only the cubic anharmonic term in crystal potential energy, the linewidth $\Gamma_j^{(3)}(\omega)$ due to the cubic term can be expressed as follows

$$\Gamma_j^{(3)}(\omega) = -18\frac{\pi}{\hbar^2}\sum_{q_1}\sum_{j_1,j_2} |V(0j;q_1j_1;-q_1j_2)|^2 \{n_{j_1}(q_1) + n_{j_2}(-q_1) + 1\}$$

$$\times [\delta(\omega + \omega_{j_1}(q_1) + \omega_{j_2}(-q_1)) - \delta(\omega - \omega_{j_1}(q_1) - \omega_{j_2}(-q_1))]$$

$$+ 2(n_{j_1}(q_1) - n_{j_2}(-q_1)))\delta(\omega - \omega_{j_1}(q_1) - \omega_{j_2}(-q_1))\}. \tag{1}$$

Here, $n_j(q) = [\exp(\hbar\omega_j/kT) - 1]^{-1}$ is the phonon occupation number and $V(0j;q_1j_1;$ $-q_1j_2)$ is the cubic anharmonic coefficient of the crystal potential. As the calculation

Table 1. Parameters used to calculate the phonon dispersion curves.

Parameters and short range force constants (unit: e^2/v)			
$A_1 = 80 \cdot 1$	$A_2 = 196 \cdot 6$	$A_3 = 17 \cdot 0$	$A_4 = 31 \cdot 3$
$B_1 = -26 \cdot 8$	$B_2 = -62 \cdot 3$	$B_3 = 11 \cdot 6$	$B_4 = 2 \cdot 9$
Effective charge (unit: e)			
$Ge = 2 \cdot 32$		$O = -1 \cdot 16$	
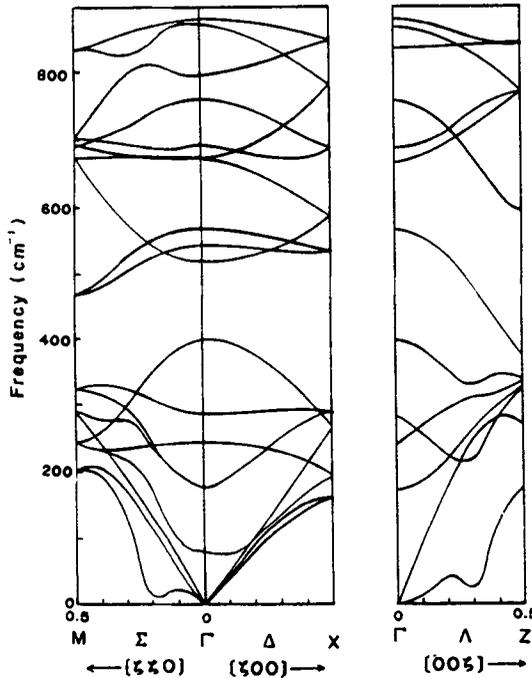
Figure 2. Phonon dispersion curves in the direction of (100), (110) and (001), calculated using the rigid ion model according to Katiyar and Krishnan (1969).

would be tedious the anharmonic coefficient $V(0j; q_1 j_1; -q_1 j_2)$ is considered to be independent on variables $0j, q_1 j_1$ and $-q_1 j_2$ and a constant and an ajustable parameter was obtained to fit the data by using the same consideration as reported earlier (1983). Therefore, $\Gamma_j^{(3)}(\omega)$ may be written as

$$\Gamma_j^{(3)}(\omega) = A \sum_{q_1} \sum_{j_1, j_2} \frac{1}{\omega_j(0)\omega_{j_1}(q_1)\omega_{j_2}(-q_1)} \{(n_{j_1}(q_1) + n_{j_2}(-q_1) + 1)$$
$$\times [\delta(\omega + \omega_{j_1}(q_1) + \omega_{j_2}(-q_1)) - \delta(\omega - \omega_{j_1}(q_1) - \omega_{j_2}(-q_1))]$$
$$+ 2(n_{j_1}(q_1) - n_{j_2}(-q_1))\delta(\omega - \omega_{j_1}(q_1) + \omega_{j_2}(-q_1))\}. \qquad (2)$$

The summation term except the constant A in (2) can be identified as two-phonon density of states. Thus the two-phonon density of states is expressed as

$$\sum_{q_1} \sum_{j_1,j_2} \frac{1}{\omega_j(0)\omega_{j_1}(q_1)\omega_{j_2}(-q_1)} \{(n_{j_1}(q_1) + n_{j_2}(-q_1) + 1)[\delta(\omega + \omega_{j_1}(q_1)$$
$$+ \omega_{j_2}(-q_1)) - \delta(\omega - \omega_{j_1}(q_1)\omega_{j_2}(-q_1))] + 2(n_{j_1}(q_1) - n_{j_2}(-q_1))$$
$$\times \delta(\omega - \omega_{j_1}(q_1) + \omega_{j_2}(-q_1))\}. \tag{3}$$

Using the phonon dispersion curves, the two-phonon density of states was calculated by taking the summations over wave vector q 1331 points in the Brillouin zone. δ function was approximated as follows

$$\delta(x) = \lim_{\varepsilon \to +0} \frac{1}{\pi} \frac{\varepsilon}{x^2 + \varepsilon^2}, \tag{4}$$

where ε was taken as 10. The two-phonon density of states with $600 \sim 800 \, \mathrm{cm}^{-1}$ region at 300 and 1000 K is shown in figure 3. The observed linewidths $\Gamma_j(\omega)$ with temperatures show slow change, and approximately linear. Therefore, $\Gamma_j^{(3)}(\omega)$ due to the cubic anharmonic term only is considered for comparison with the observed linewidths. The constant A for A_{1g} mode was taken as $4\cdot4 \times 10^5 \, \mathrm{cm}^{-1}$. As seen in figure 4, the calculated linewidths agree with the observed values. The accuracy for $\Gamma_j(\omega)$ was within $\pm 4\%$. If the quartic term contributes only to $\Gamma_j(\omega)$, the values of linewidths are expected to change from about 4·5 to 45 cm^{-1}, over the temperature range of 300–1000 K. Therefore, the contribution to the linewidths due to quartic term may be considered small and hence the temperature dependence of Raman linewidths
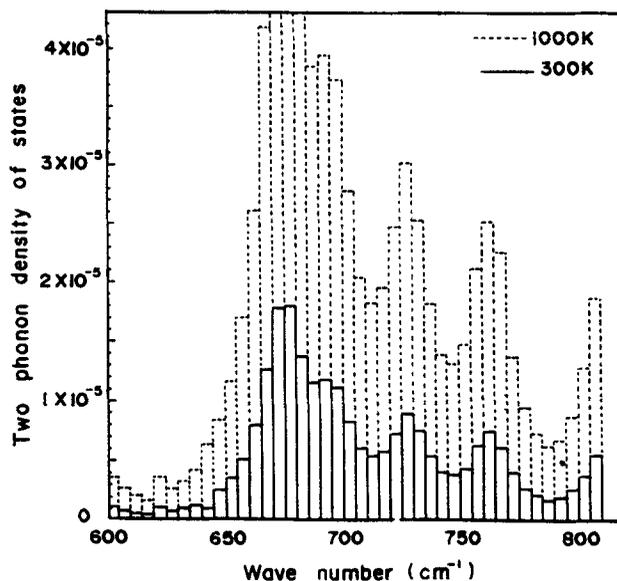

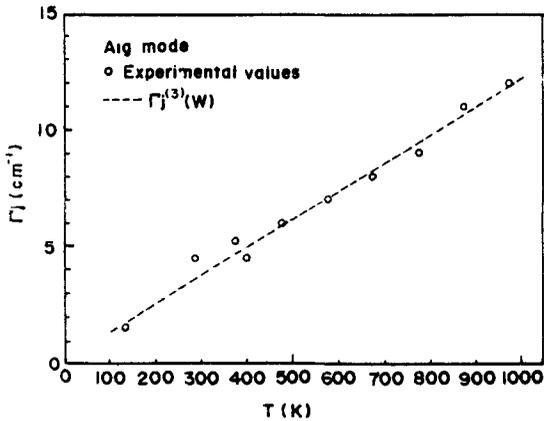**Figure 3.** The two phonon density of states with wavenumbers.

Figure 4. The linewidths for the A_{1g} mode with temperatures. The observed values are shown by the open circles, and the calculated values are shown by the dashed line.

for GeO_2 powder is caused approximately by the cubic anharmonic term. More detailed calculations will be performed in future.

4. Conclusion

The Raman spectrum for A_{1g} mode of GeO_2 powder was measured at temperature range of 130 to 973 K and the linewidths at various temperatures were obtained. The phonon dispersions for GeO_2 were calculated, and the temperature dependence of the Raman linewidths was analysed by considering the two-phonon density of states due to the cubic anharmonic term. The values of A for $\Gamma_j^{(3)}(\omega)$ were taken and the experimental and calculated values for $\Gamma_j(\omega)$ show good agreement. From this it is concluded that the temperature dependence of the linewidth for GeO_2 powder can be explained by considering the cubic anharmonic term of the crystal potential energy and is governed by the phonon occupation number.

Acknowledgement

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