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Abstract. The first-order Raman spectrum for the A_{1g} mode of an MgF_2 single crystal was measured at various temperatures from 301 to 973 K. The frequency shift and linewidth change significantly with increasing temperature. In order to analyse the temperature dependence of the frequency shift, first we calculated the anharmonic force constants of an MgF_2 crystal. Then applying the lattice-dynamical perturbative treatment to the third- and fourth-order proper self-energy, we evaluated each contribution from the cubic and quartic anharmonic terms to the whole shift and could explain the frequency shift throughout the whole range of temperatures. We found that the cubic as well as quartic anharmonic terms play an important role in the temperature dependence of the Raman frequency shift for the A_{1g} mode.

1. Introduction

The temperature dependences of the linewidth and frequency shift of the normal vibration of several crystals pose a very interesting problem and they have been examined by various workers from different points of view [1–12, 14–17, 28, 29]. In these investigations, it has been shown that the cubic and quartic anharmonic terms of the crystal potential energy play important roles in these phenomena. However, there is some difficulty in explaining the contribution of the cubic or quartic anharmonic term to the Raman linewidth and frequency shift as a function of temperature, which generally depends on the crystal structure and vibrational mode. Balkanski et al [13] have applied the lattice-dynamical perturbative method to silicon with the diamond structure and showed that the cubic and quartic anharmonic terms are necessary to describe the temperature dependences of the frequency shift and the linewidth of the LO-mode Raman spectrum.

We have already calculated the temperature dependence of the linewidth of the A_{1g} mode for an MgF_2 crystal with a lattice-dynamical perturbative treatment including cubic and quartic anharmonic terms [26] but have not performed an analysis of the temperature dependence of frequency shift of the A_{1g} mode for this crystal. In this paper we shall try to explain the Raman frequency shift of the A_{1g} mode of an MgF_2 crystal from the above point of view. In section 2, we shall refer briefly to the experimental method. In section 3, we shall derive the anharmonic force constants of the rutile structure which are used to calculate the proper self-energy part due to phonons. A comparison of the theoretical calculations with the experimental data is given in section 4, and the anharmonic contribution to the Raman shift in an MgF_2 crystal is discussed in detail.

2. Experimental details

The primitive unit cell of the rutile structure is shown in figure 1, where the atoms are labelled according to Porto *et al* [10]. The two positive (magnesium) ions occupy the positions $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, c/2a)a$, and the four negative (fluoride) ions occupy the positions $(u, u, 0)a$, $(1-u, 1-u, 0)a$, and $(\frac{1}{2} \pm u, \frac{1}{2} \mp u, c/2a)a$, where a and c are lattice parameters and u is the fractional atomic coordinate [18]. The rutile structure has the symmetry of the space group D_{4h}^{14} ($P4_2/mnm$). The Raman-active modes are B_{1g} (Γ_3^+), E_g (Γ_5^-), A_{1g} (Γ_1^+) and B_{2g} (Γ_4^+) [10]. Among these modes, we have chosen the A_{1g} mode because its intensity is rather strong. The MgF$_2$ single crystal used in this experiment was obtained from Oyo Koken Co., cut parallel and perpendicular to the c axis and optically polished; it measured 4 mm × 4 mm × 5 mm (c axis) and its purity was over 99.99%. An argon ion laser of wavelength 4880 Å was used as the Raman exciting source. The laser beam was directed upon the (1,0,0) plane of the specimen in the Nichrome furnace with an internal diameter of 15 mm and a length of 100 mm which changes the temperature from 301 to 973 K. The scattering light from the (0,1,0) plane was measured with a laser Raman spectrometer (model U1-UV, produced by Nippon Denshi Co.) equipped with a photon-counting system. The calibration of the wavelength was carried out with a plasma line of the Ar ion tube. The accuracy of the wavelength was 0.5 Å (± 2 cm^{-1}). Raman measurements were performed in a wide range of temperatures. In order to remove the effects of different experimental conditions, we have performed a deconvolution of the actual Raman intensity function with the response function of the spectrometer by a Lorentzian shape and obtained the real linewidth and the frequency shift from the observed spectrum.
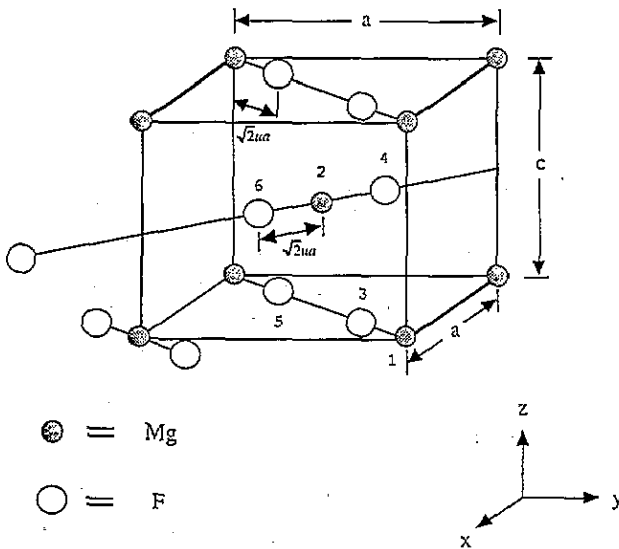

Figure 1. The tetragonal unit cell for the magnesium fluoride crystal, where the atoms are labelled according to the notation of Porto *et al* [10].

3. Anharmonic force constants

The frequency shift $\Delta\omega_{obs}$ observed at the temperature T is made up of a contribution $\Delta\omega_0$ from the thermal expansion and a purely anharmonic contribution $\Delta\omega_A$:

$$\Delta\omega_{obs} = \Delta\omega_0 + \Delta\omega_A. \tag{1}$$

According to Liarokapis *et al* [19] and Raptis *et al* [20], the first term in equation (1) can be calculated directly from the following equation:

$$\Delta\omega_0(T) = -\int_0^T \frac{\beta}{\kappa}\left(\frac{\partial\omega}{\partial P}\right)_T dT' \tag{2}$$

where $\kappa(T)$ is the volume compressibility and $\beta(T)$ is the volume thermal expansion coefficient. On the other hand, in the lattice-dynamical perturbative treatment [7–13], the purely anharmonic contribution $\Delta\omega_A(0, j: \Omega)$ is given by the real part of the proper self-energy shown in figure 2 including quartic anharmonic terms of up to second order and expressed as

$$\Delta\omega_A(0, j; \Omega) = \Delta\omega^{(3)}(0, j; \Omega) + \Delta\omega^{(4a)}(0, j; \Omega) + \Delta\omega^{(4b)}(0, j; \Omega) + \Delta\omega^{(4c)}(0, j; \Omega) \tag{3}$$

where we have employed the same notation and expression as used by Balkanski *et al* [13] for each term appearing in equation (3); so we shall not repeat the rather complex definition. The Fourier-transformed anharmonic constants are given as

$$V(\lambda_1 \ldots \lambda_s) = (1/2S!)(\hbar/2N)^{S/2}N\Delta(q_1 + \ldots + q_s)[\omega_{j_1}(q_1)\ldots\omega_{j_s}(q_s)]^{-1/2}C(\lambda_1 \ldots \lambda_s) \tag{4}$$

where $\Delta(q_1 + \ldots + q_s)$ indicates the momentum conservation at each vertex ($\Delta(q) = 1$ if q is a reciprocal-lattice vector and is otherwise 0, and λ_j is the jth phonon branch at the wavevector q. According to Ipatova and co-workers [7, 16] the coefficients $C(\lambda_1 \ldots \lambda_s)$ are slowly varying functions with their arguments in general and are therefore assumed to be constant and equal to C_s.
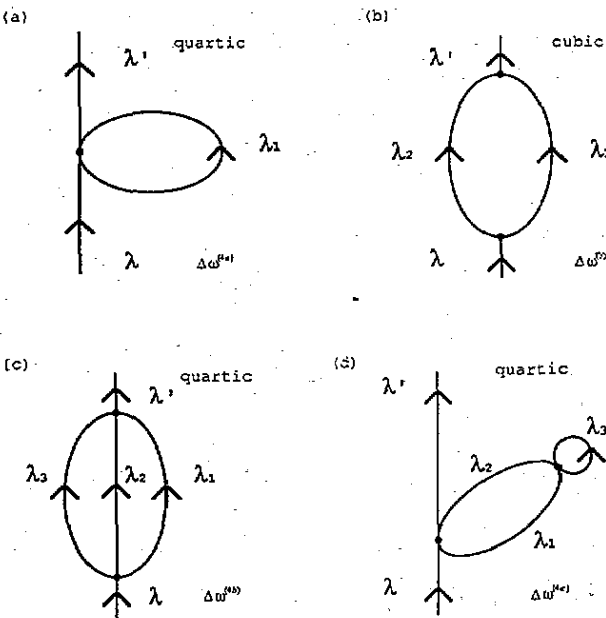

Figure 2. Diagrams of proper self-energy which contribute to the frequency shift $\Delta\omega_A$ [13], where λ_1 is the collective index for $\omega_{j_1}(q_1)$.

In order to calculate the temperature dependence of the Raman shift, the cubic and quartic coefficients C_s of central short-range force were derived for the rutile structure on

the assumption that there are no Coulomb anharmonicities. As mentioned before, there are four proper self-energy diagrams up to second order contributing to the temperature dependence of the Raman shift shown in figure 2. The anharmonic coefficients $|C_3|^2$ and $|C_4|^2$ corresponding to figures 2(b) and 2(c), respectively, have the same expressions as in [26] and play an important role in the temperature dependences of both the Raman linewidth and the shift. On the other hand, with respect to the frequency shift, figures 2(a) and 2(d) should be considered. Thus we have to calculate the new anharmonic coefficients $|C_4'|$ and $|C_4''|$ corresponding to figures 2(a) and 2(d), respectively. After performing tedious calculations according to Ipatova and co-workers [7, 16], we obtained new expressions for the anharmonic coefficients:

$$|C_4'| = [1/\omega_j^2(0)\mu_2]C_{4M}'(C_{4C}'^A + 2C_{4C}'^B) \tag{5}$$

$$|C_4''| = \frac{1}{\omega_j^2(0)\mu_2 S_3}[C_{4M}''^A(C_{4C}''^A + 2C_{4C}''^B + 2C_{4C}''^C + 2C_{4C}''^D)$$
$$+ C_{4M}''^B\{C_{4C}''^E + 2C_{4C}''^F + C_{4C}''^G + 4(C_{4C}''^H + 2C_{4C}''^I)\}] \tag{6}$$

where μ_2 and S_3 are defined by [7]

$$\mu_2 = \frac{1}{N}\sum_{qj}\omega_j^2(q) \tag{7}$$

$$S_3 = \frac{1}{N}\sum_q\sum_{jj'}\omega_j^2(q)\omega_{j'}^2(q). \tag{8}$$

Here the coefficients in equations (5) and (6) involve derivatives of potential that can be defined as follows:

$$C_{4M}' = \tfrac{8}{3}(1/M_1 + 1/M_2)^2 \tag{9}$$

$$C_{4C}'^A = r_1^4 A_1' + 14r_1^2 B_1' + 27C_1' \tag{10}$$

$$C_{4C}'^B = r_2^4 A_2' + 10r_2^2 B_2' + 15C_2' \tag{11}$$

$$C_{4M}''^A = \tfrac{64}{3}(M_1 + M_2)^2(M_1^2 + M_2^2)/M_1^4 M_2^4 \tag{12}$$

$$C_{4M}''^B = \tfrac{16}{3}(M_1 + M_2)^2/M_1^3 M_2^3 \tag{13}$$

$$C_{4C}''^A = r_1^2 B_1' + 5C_1' \tag{14}$$

$$C_{4C}''^B = t_2^2 r_2^4 A_2' + (7t_2^2 + 1)r_2^2 B_2' + 5C_2' \tag{15}$$

$$C_{4C}''^C = \tfrac{1}{2}(r_1^4 A_1' + 13r_1^2 B_1' + 22C_1') + 2[t_1^2 r_2^4 A_2' + (7t_1^2 + 1)r_2^2 B_2' + 5C_2'] \tag{16}$$

$$C_{4C}''^D = \tfrac{1}{2}(r_1^4 A_1' + 7r_1^4 B_1') - 2(t_1^2 r_2^4 A_2' + 7t_1^2 r_2^2 B_2') \tag{17}$$

$$C_{4C}''^E = r_1^4 A_1' + 13r_1^2 B_1' + 22C_1' \tag{18}$$

$$C_{4C}''^F = r_1^2 B_1' + 5C_1' \tag{19}$$

$$C_{4C}''^G = r_1^4 A_1' + 7r_1^2 B_1' \tag{20}$$

$$C_{4C}''^H = r_2^8 A_2'^2 + 66r_2^4 B_2'^2 + 75C_2'^2 \tag{21}$$

$$C_{4C}''^I = 8r_2^6 A_2' B_2' + 5r_2^4 A_2' C_2' + 50r_2^2 B_2' C_2' \tag{22}$$

Table 1. Parameters used to calculate the phonon frequency $\omega_j(q)$ [18].

Short-range force constants (in units of $e^2/2v$)			
$A_1 = 71.596$	$A_2 = 72.356$	$A_3 = 4.172$	$A_4 = 16.915$
$B_1 = -9.022$	$B_2 = -7.356$	$B_3 = 0.030$	$B_4 = -1.542$
Effective charge (in units of e)			
Mg, 1.58	F, -0.79		

where, using atomic positions and atomic distances in terms of lattice parameters a and c and atomic parameter u, the parameters r_1, r_2, t_1 and t_2 are defined by

$$r_1 = \sqrt{2}ua \qquad r_2 = a[2(\tfrac{1}{2} - u)^2 + c^2/4a^2]^{1/2}$$
$$t_1 = (1/r_2)a(-\tfrac{1}{2} + u) \qquad t_2 = (1/r_2)a(-c/2a). \tag{23}$$

The dimensionless parameters t_1 and t_2 satisfy the following relation:

$$2t_1^2 + t_2^2 = 1. \tag{24}$$

The coefficients A_1, A_2, B_1, B_2, C_1 and C_2 involve derivatives of potential up to third and fourth order and can be obtained for our model as

$$A_1' = (1/r_1^4)[\phi^{IV}(r_1) - (6/r_1)\phi^{III}(r_1) + (15/r_1^2)\phi^{II}(r_1) - (15/r_1^3)\phi^{I}(r_1)] \tag{25}$$

$$A_2' = (1/r_2^4)[\phi^{IV}(r_2) - (6/r_2)\phi^{III}(r_2) + (15/r_2^2)\phi^{II}(r_2) - (15/r_2^3)\phi^{I}(r_2)] \tag{26}$$

$$B_1' = (1/r_1^3)[\phi^{III}(r_1) - (3/r_1)\phi^{II}(r_1) + (3/r_1^2)\phi^{I}(r_1)] \tag{27}$$

$$B_2' = (1/r_2^3)[\phi^{III}(r_2) - (3/r_2)\phi^{II}(r_2) + (3/r_2^2)\phi^{I}(r_2)] \tag{28}$$

$$C_1' = (1/r_1^2)[\phi^{II}(r_1) - (1/r_1)\phi^{I}(r_1)] \tag{29}$$

$$C_2' = (1/r_2^2)[\phi^{II}(r_2) - (1/r_2)\phi^{I}(r_2)]. \tag{30}$$

Using the above anharmonic coefficients, the temperature dependence of the Raman frequency shifts $\Delta\omega_A$ solely due to the anharmonic terms was calculated.

4. Calculation of the frequency shifts

The normal mode frequency $\omega_j(q)$ for an MgF₂ crystal was first calculated using the same parameters and applying the same method for the rigid-ion model as described by Katiyar and Krishnan [11]. In the present paper, the normal mode frequency $\omega_j(q)$ was calculated for one sixteenth of the first Brillouin zone (figure 3). Therefore the wavevector $q = (\pi n_x/10a, \pi n_y/10a, \pi n_z/10c)$ satisfies the conditions

$$0 \leqslant n_y \leqslant n_x \leqslant 10 \qquad 0 \leqslant n_z \leqslant 10 \tag{31}$$

where n_x, n_y and n_z are integers. There are 726 sets of wavevectors in this region, and 9261 sets can all be expanded in the first Brillouin zone by symmetry. We have used the same values as Katiyar [18] for the force constants and effective charges (table 1) in the calculations of the normal mode frequency $\omega_j(q)$ in all the first Brillouin zone. The dispersion curves were checked in the direction $q(1, 0, 0)$, $q(1, 1, 0)$ and $q(0, 0, 1)$ and agree with the results of Katiyar [18]. The calculated 'phonon energy surface' in the q_x–q_y plane ($q_z = 0$) of the Γ_1^+ (A₁g) mode in the first Brillouin zone is presented in figure 4.

typical points in the first
Brillouin zone

Γ = (0, 0, 0)
X = (π/a, 0, 0)
M = (π/a, π/a, 0)
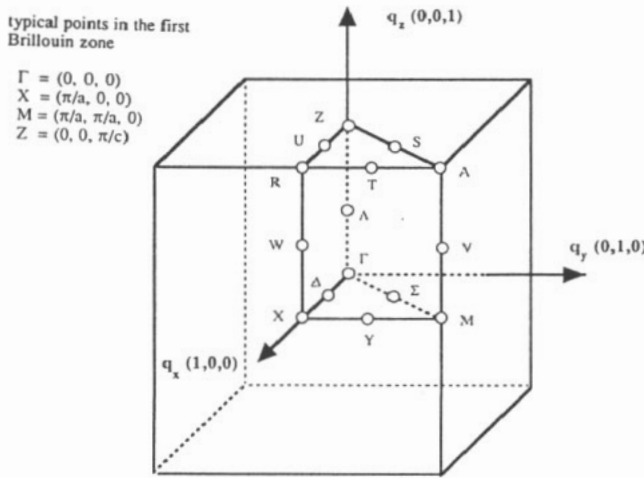Z = (0, 0, π/c)

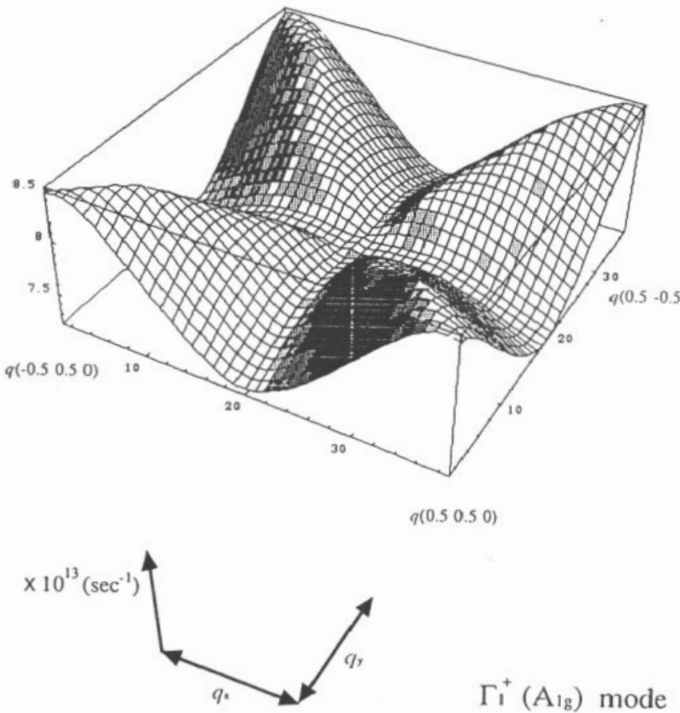**Figure 3.** Brillouin zone of the MgF$_2$ crystal [11, 18].

Figure 4. Calculated phonon energy surface of the Γ_1^+ (A$_{1g}$) mode.

Next, we shall estimate the frequency shift $\Delta\omega_0$ due to the thermal expansion using equation (2) which can be expressed under the assumption that the isothermal mode Grüneisen parameter γ_{mode} is temperature independent [19, 20] as

$$\Delta\omega_0 \simeq -\omega_j(0)\gamma_{mode}\int_0^T \beta(T')\,dT' \tag{32}$$

where we take $\omega_j(0)$ as 413 cm^{-1} from the experimental results of Browder [21] at a very low temperature (about 16 K). On the other hand, Liarokapis et al [19] and Raptis et al

[20] have shown that the volume thermal expansion coefficient β is covered well by the analytical form [19, 20]

$$\beta(T) = (A/T + B/T^2)\sinh^{-2}(T_1/T). \tag{33}$$

We have applied equation (33) to the experimental results of Browder [21] in the temperature range 16–310 K. The best values of the constants A, B and T_1 are obtained as $A = 2.727\,86 \times 10^{-3}$, $B = 1.395\,08$ K and $T_1 = 240$ K (shown by the full curve in figure 5). On the other hand, Pascusal *et al* [22] have estimated some values of the mode Grüneisen parameter $\gamma_{A_{1g}}$ as 2.2 (rigid-ion model) and 2.4 (shell model) theoretically and 2.3 ± 0.2 from the uniaxial stress experiment, while Streiffer and Barsh [23] give the value 1.24 from theoretical calculation. Therefore, we regard the temperature-independent isothermal mode Grüneisen parameter $\gamma_{A_{1g}}$ as an adjustable constant in the calculation of equation (3) [20, 24, 25]. The theoretical and experimental values of the Raman frequency shift of the A_{1g} mode versus temperature for the MgF₂ crystal are presented in figure 6, including up to quartic anharmonic terms with the thermal expansion contribution $\Delta\omega_0$. We have chosen the value of the mode Grüneisen parameter $\gamma_{A_{1g}}$ as 1.95 to fit the experimental results in figure 6 because the introduced mean error of about 10% will not affect the general character of the results [20, 24, 25]. This calculation has been carried out on an HP730 (UNIX) computer. The calculated values of cubic and quartic anharmonic contribution to the frequency shift $\Delta\omega_A$ which correspond to figure 2 [13, 29] are presented in figure 7 in the temperature range 100–1000 K.
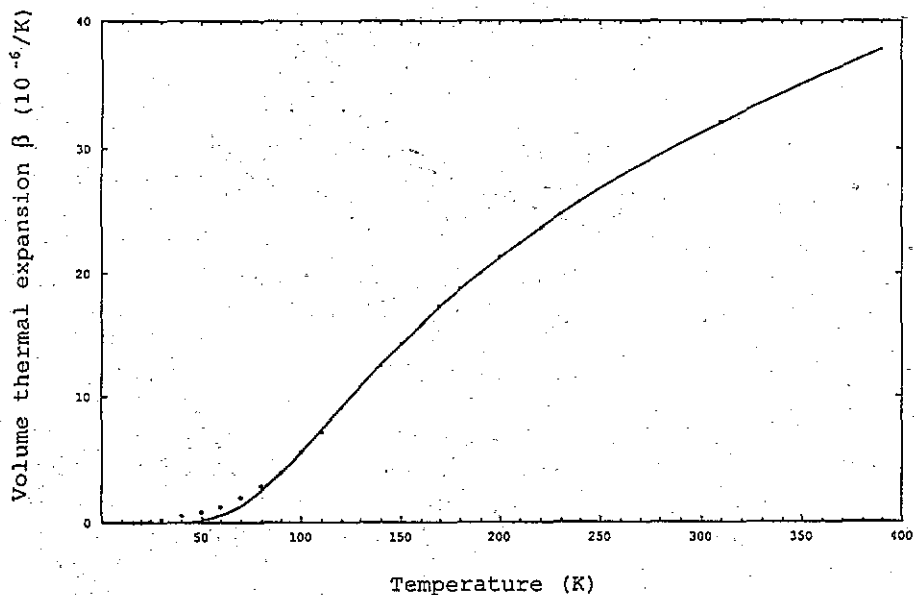

Figure 5. The volume thermal expansion coefficients $\beta(T)$ for the MgF₂ crystal: ——, theoretical fit of equation (33); ●, observed values [21].
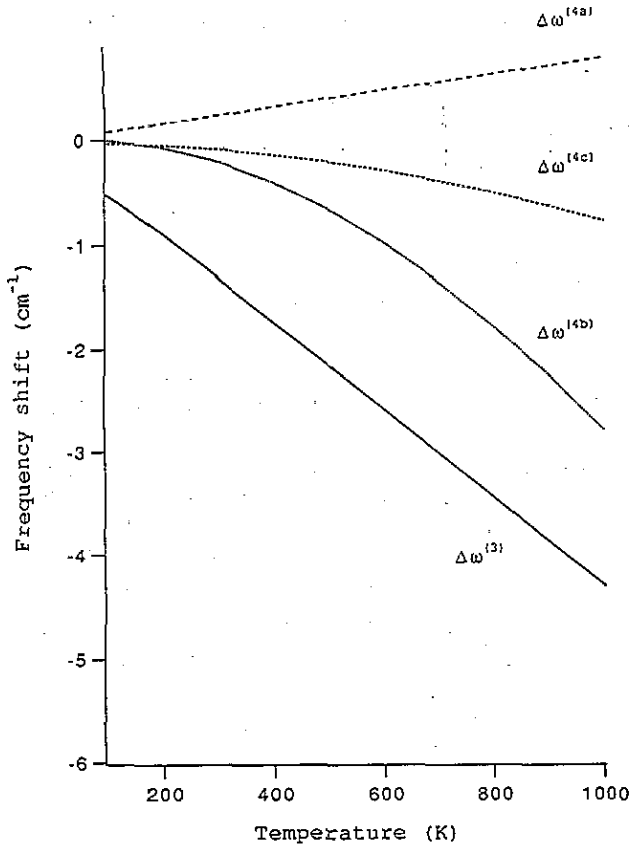
Figure 6. Calculated frequency shift due to the cubic and quartic anharmonic terms in equation (1): ●, experimental points of this work; +, observed values of Sauvajol et al [27] in the low-temperature range.

5. Conclusion

We have already performed the calculation of the temperature dependence of the linewidth of the Raman spectrum for the A_{1g} mode of an MgF_2 crystal [26]. Here, we investigated the temperature dependence of the frequency shift of this crystal by a lattice-dynamical perturbative treatment [7–13].

The contributions to the temperature dependence of the frequency shift $\Delta\omega_{obs}$ can be divided into two parts: the volume thermal expansion $\Delta\omega_0$ and the purely anharmonic terms $\Delta\omega_A$. The former was estimated by assuming the analytical form of the volume thermal expansion coefficient [19, 20]. In order to calculate the latter contribution, first we calculated the anharmonic force constants of the MgF_2 rutile structure which appear in the interaction vertex of proper self-energy. Then, a full calculation of the real part of the proper self-energy including the cubic and quartic anharmonic terms has been made, and we calculated the anharmonic contribution to the frequency shift as a function of temperature. As seen in figure 6, the experimental value shows good agreement with the theoretical results in the approximate temperature range 16–973 K. In particular, figure 7 shows that there is rough cancellation between the contributions from figures 2(a) and 2(d) to the anharmonic frequency shift $\Delta\omega_A$, and the quartic anharmonic term will play an increasingly important role with increasing temperature. The experimental and theoretical results of the temperature dependence of the Raman linewidth of the A_{1g} mode [26] also indicate the necessity of including the cubic as well as the quartic anharmonic term. Therefore we conclude that the
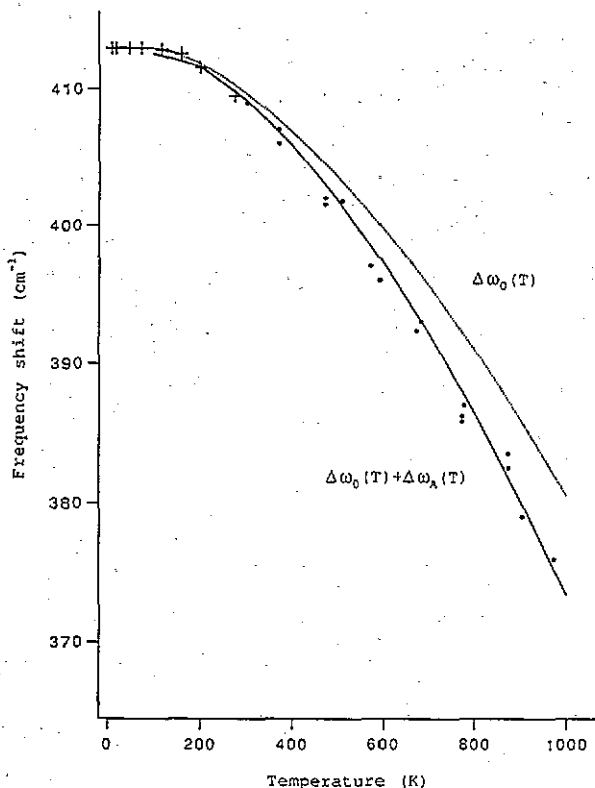
Figure 7. Calculated curves of the purely anharmonic contribution to the frequency shift from figure 2.

temperature dependence of the linewidth and frequency shift of the Raman-active A_{1g} mode for the MgF$_2$ crystal can be explained completely by taking into account both the cubic and the quartic anharmonic terms.

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