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Temperature dependence of transverse and longitudinal optic modes in the α and β phases of quartz

F. Gervais and B. Piriou

Centre de Recherches sur la Physique des Hautes Températures, Centre National de la Recherche Scientifique, 45045 Orléans Cedex, France

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The temperature dependence of the infrared reflectivity spectra (A_2- and E-type vibrational modes) of quartz is reported in the α and β phases with emphasis on the vicinity of the $\alpha \rightarrow \beta$ phase transition. Spectra have been fitted with a four-parameter dispersion model based on the factorized form of the dielectric function that allows the temperature dependence of the TO and LO frequencies and damping to be determined. Two A_2 and three E modes (among the six E modes studied here) are forbidden in the β phase, and they critically lose their polar character at the approach of the phase transition. The frequencies of a number of modes critically soften or harden in the α phase, in the vicinity of $T_c = 846$ K. A comparison with thermal lattice expansion indicates that this critical behavior might be understood in term of pure volume effect. In the α phase, mode dampings diverge in the vicinity of the transition whereas in the range 300–700 K and in the β phase, phonon lifetimes appear limited by anharmonic three-phonon coupling.

I. INTRODUCTION

Though quartz is one of the most studied material in physics, the A_2-type vibrational modes were still unknown in the β phase until, very recently, one of the authors has presented a preliminary report.[1] Quartz is well-known to undergo an $\alpha - \beta$ phase transition at $T_c = 846$ K. The soft mode associated to this transition has been shown to be of the A_1 type, that is Raman-active only.[2-5] The temperature dependence of the A_1-type modes has been reported incidentally[3] due to the interest in the study of the soft mode. The frequencies of the E-type modes—both Raman and infrared active—were reported[6] in the β phase by Raman scattering, but most longitudinal optical (LO) frequencies were not observed. On the other hand, anomalous behaviors of A_2-type modes[1,7] and mainly of the two lowest-frequency phonon branches[8] have been pointed out in the α phase, at the approach of the phase transition.

The purpose of this paper is to analyze the temperature dependence of the A_2- and E-type modes, particularly in the vicinity of the transition, and to try to answer the question whether the anomalous behaviors that will be reported in detail presently may be understood in term of quasiharmonic or anharmonic effects. Mode damping will be studied also because anharmonicity cannot be neglected at temperatures as high as 846 K. Infrared reflectivity spectroscopy appears as a powerful technique for this kind of study. An advantage of this method is its sensitivity in the measurement of the TO and LO frequencies in the case of very weak splitting. Several LO and TO lines indeed overlap in Raman spectra. Frequencies and damping of TO modes but also frequencies and damping of LO modes can be deduced from reflectivity data by using a four-parameter semiquantum model (FPSQ).[9-11]

Apart from a qualitative study[12] performed at a time where the methods of analysis of reflection spectra by computers were not yet available, infrared reflection spectra of α-quartz were reported at room temperature only by Spitzer and Kleinman[13] and analyzed by the Kramers-Kronig method and classical dispersion theory, and by the authors at two other temperatures for the A_2 modes only.[7]

II. REFLECTIVITY DATA AND ANALYSIS

The experimental procedure is that presented in Ref. 11. A small electric furnace is sufficient to heat the sample up to 1000 K. The temperature dependence of infrared reflection spectra is shown in Figs. 1 and 2 for the A_2- and E-type modes, respectively. Room temperature data are in agreement within experimental error with those reported previously.[13] A_2 modes labeled 1 and 3 and E modes labeled 3, 5, and 8 in the present work are forbidden in the β phase[14] and they do disappear by passing the $\alpha - \beta$ phase transition.

Spectra have been fitted with the aid of the following formulas[10,11]

$$R = \left| (\sqrt{\epsilon} - 1)/(\sqrt{\epsilon} + 1) \right|^2 , \quad (1)$$

$$\epsilon = \epsilon_\infty \prod_j \frac{\Omega_{j\mathrm{LO}}^2 - \omega^2 + i\gamma_{j\mathrm{LO}}\omega}{\Omega_{j\mathrm{TO}}^2 - \omega^2 + i\gamma_{j\mathrm{TO}}\omega} , \quad (2)$$

where $\Omega_{j\mathrm{TO}}$, $\gamma_{j\mathrm{TO}}$, $\Omega_{j\mathrm{LO}}$, $\gamma_{j\mathrm{LO}}$ are the frequencies and damping of the transverse and longitudinal optic modes, respectively. ϵ_∞ is the "high-frequency" contribution to the dielectric function. Very good fits to the reflectivity data are achieved as shown in Figs. 1 and 2. Parameters used are listed in Tables I and II.

A first approach with the aid of the classical dispersion formula,[13] though giving less good fits in the low-frequency range at temperatures intermediate between 700 and 846 K, provides the classical TO oscillator strengths $\Delta\epsilon_j$ which are related to the TO-LO splitting. Values found for $\Delta\epsilon_j$ as a function of temperature are also listed in Tables I and II.

Two among the three additional oscillators introduced by Spitzer *et al.*[13] to fit the extraordinary ray (A_2 modes) and the one introduced to fit the ordinary ray (E modes) are no longer necessary if the TO and LO damping may be different as allowed by the FPSQ model.[10,11] Both dampings are implicitly assumed to be equal by the classical three-parameter model,[10] and when the LO mode decays with a shorter lifetime than does the TO mode, the procedure was indeed to add a weak overdamped oscillator considered as a multiphonon absorption in the vicinity of the LO frequency. A comparison of frequencies indicates that the third small feature in the A_2 spectrum near 500 cm^{-1}, treated as an additional oscillator as in Ref. 13, possibly is the $E^{(4)}$ (LO) mode which would be weakly active due to imperfect polarization. Very weak oscillators indeed are most sensitively observed at the top of an infrared band.

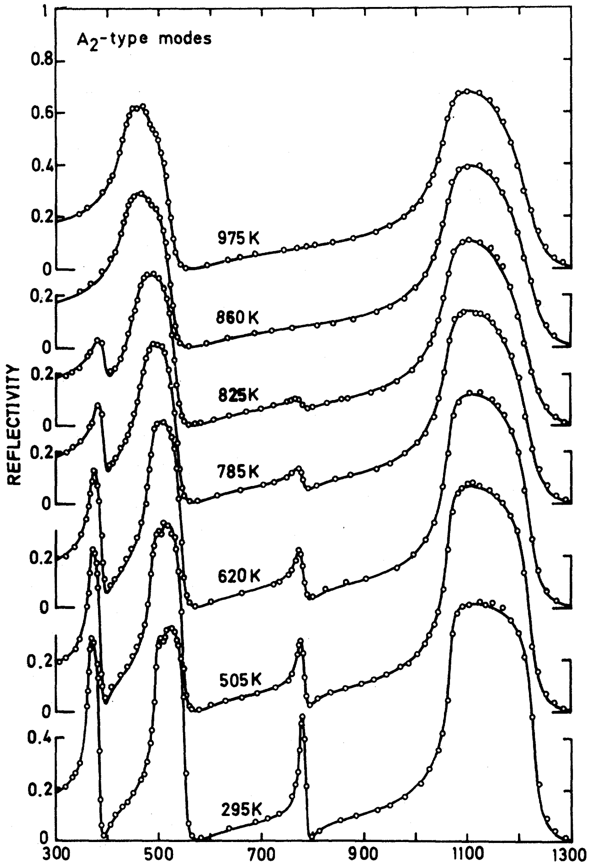

FIG. 1. Temperature and frequency dependence of the infrared reflectivity (open circles) for the extraordinary ray in the α and β phases of quartz ($T_c = 846$ K). A fit (full curves) to the data with the aid of the four-parameter semiquantum model.

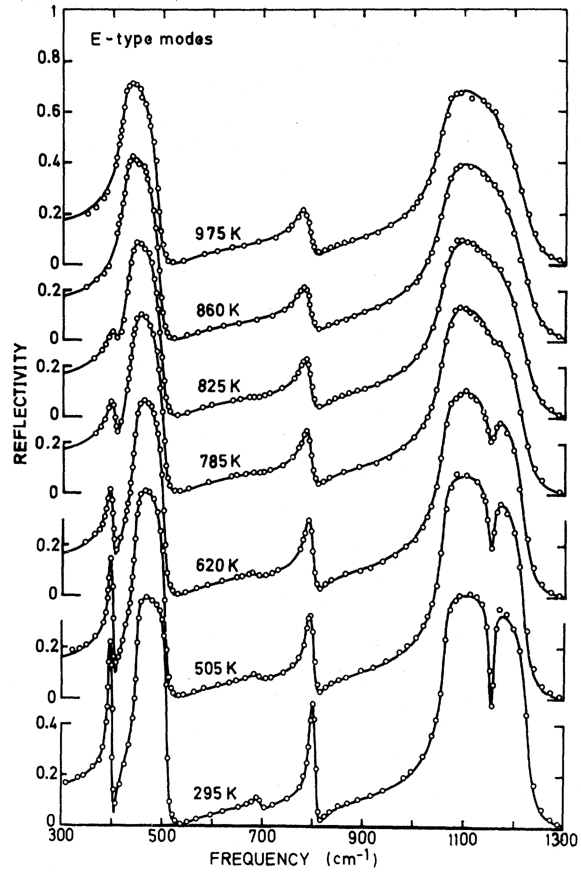

FIG. 2. Experimental infrared reflectivity (open circles) for the ordinary ray. Full curves are best fit of Eq. (2) to the data.

Our data for the E modes at room temperature are compared with other infrared[13,15] and Raman[3,6,16-19] data in Table III. The TO-LO splitting of modes 5 and 8 is well determined by infrared technique, whereas a single line is observed in Raman spectra. The agreement with existing infrared data is satisfactory. A comparison with the most complete set of Raman data[17] shows agreement within 0.3% for all frequencies. The agreement for damping is poorer. This is not surprising in view of the large uncertainty indicated for the Raman linewidths. Besides, damping is less accurately measured at room temperature than at high temperature in the case of wide infrared bands. Nevertheless the result $\gamma_{7\mathrm{LO}} > \gamma_{7\mathrm{TO}}$ found by both techniques indicates different phonon decays for TO

TABLE I. Parameters used to fit the infrared reflectivity spectra (A_2-type modes) as a function of temperature with the aid of the four-parameter semiquantum model [Eq. (2)]. The oscillator strengths added in the right side of the table have been obtained in a first approach by using the three-parameter summation formula Frequencies and damping of TO modes are the same in both kinds of fits.

	j		$\Omega_{j\mathrm{TO}}$ (cm^{-1})	$\gamma_{j\mathrm{TO}}$ (cm^{-1})	$\Omega_{j\mathrm{LO}}$ (cm^{-1})	$\gamma_{j\mathrm{LO}}$ (cm^{-1})	$\Delta\epsilon_j$
A_2	1	T_1	363.5	4.8	386.7	4.8	0.67
		T_2	367.7	9	390	9	0.67
		T_3	370	13	392	13	0.65
		T_4	381	17	395	17	0.51
		T_5	385	24	397	24	0.40
	2	T_1	495	5.2	551.5	5.8	0.65
		T_2	488	10.5	547.5	9	0.67
		T_3	483.5	13.5	546	12	0.81
		T_4	468.5	25	539	18	0.96
		T_5	457	31	536	19	1.12
		T_6	436.5	34	528	25	1.57
		T_7	435	30	527	27	1.58
	3	T_1	777	6.7	790	6.7	0.11
		T_2	776	12	787	12	0.09
		T_3	774.5	16	786	16	0.09
		T_4	776	20	782.5	20	0.055
		T_5	777	24	781	24	0.033
	4	T_1	1071	6.8	1229	12	0.66
		T_2	1067	10.3	1223	19	0.65
		T_3	1068	14.3	1225	26	0.66
		T_4	1063.5	23	1224	40	0.70
		T_5	1064	27	1227	48	0.71
		T_6	1064.5	29	1230	52	0.74
		T_7	1061	31.5	1227	55	0.73
additional weak oscillator		T_1	509	14	(507.5)	14	(0.03)
		T_2	504	20	(502)	20	(0.04)
		T_3	503	25	(502.5)	25	(0.007)
		T_4	499	30	(498.5)	30	(0.004)
		T_5	490	30	(489)	30	(0.004)
		T_6	490	31	(489)	31	(0.01)
		T_7	488	32	(487)	32	(0.008)

$\epsilon_\infty = 2.383$ (295 K) $\epsilon_\infty = 2.44$ (β phase)

$T_1 = 295$ K, $T_5 = 825$ K,
$T_2 = 505$ K, $T_6 = 860$ K,
$T_3 = 620$ K, $T_7 = 975$ K.
$T_4 = 785$ K,

and corresponding LO modes when the frequencies have the largest splitting. Our frequencies agree within 1% with those of Bates *et al.*,[6] who performed measurements at 805, 883, and 973 K. Moreover, the agreement for the *shifts* of frequency is better. Raman linewidths observed[6] at 883 K agree well with our infrared damping. Also the frequency shifts from room temperature down to liquid helium temperature reported by Tekippe *et al.*[18] are quite consistent with the present shifts found at higher temperatures.

The calculation of the static dielectric constant with the aid of the generalized Lyddane-Sachs-Teller relation [by putting $\omega = 0$ in Eq. (2)] yields $\epsilon_\parallel(0) = 4.5$ and $\epsilon_\perp(0) = 4.4$ at room temperature, if in the latter case the oscillator strengths of the two lowest-frequency E modes are taken into account.[20] These results are to be compared with the extrapolation of the far-infrared data[20] which yields $\epsilon_\parallel(0) = 4.64$ and $\epsilon_\perp(0) = 4.43$, together with the values $\epsilon_{s\parallel} = 4.64$ and $\epsilon_{s\perp} = 4.52$ measured at 1000 Hz.[21]

III. DISCUSSION OF THE RESULTS

A. Oscillator strengths

Inspection of Tables I and II indicates that modes forbidden in the β phase lose their polar character at the approach of the phase transition, as pointed out previously for the mode $A_2^{(3)}$.[7] As discussed in a previous paper (Ref. 11, Sec. VIII) the polar character of a mode is better described in terms

TABLE II. Parameters used to fit the infrared reflectivity data for the E modes with the FPSQ model. The oscillator strengths added in the Table are deduced from another fit by using the classical dispersion model.

	j		$\Omega_{j\mathrm{TO}}$ (cm^{-1})	$\gamma_{j\mathrm{TO}}$ (cm^{-1})	$\Omega_{j\mathrm{LO}}$ (cm^{-1})	$\gamma_{j\mathrm{LO}}$ (cm^{-1})	$\Delta\epsilon_j$
E	3	T_1	393.5	2.8	402	2.8	0.33
		T_2	394.5	5.7	403	5.7	0.33
		T_3	394	9.8	402	9.8	0.33
		T_4	396	14	402.5	14	0.30
		T_5	400	15	403.7	15	0.22
	4	T_1	450	4.5	510	4.1	0.83
		T_2	445.5	8.5	506	8.5	0.84
		T_3	443	11.2	504	11	0.89
		T_4	435.5	16.5	501	15	0.96
		T_5	430	18.5	498	17	1.05
		T_6	421.5	17	494.5	17	1.30
		T_7	420	17.2	492	18	1.30
	5	T_1	695	13	697.6	13	0.02
		T_2	691	22	693	22	0.02
		T_3	687	26	689	26	0.02
		T_4	682	35	683	35	0.015
		T_5	680	36	681	35	0.01
	6	T_1	797	6.9	810	6.9	0.11
		T_2	792	11.5	805	11.5	0.11
		T_3	790.5	14.3	804.5	14.3	0.12
		T_4	785.5	18	799.5	18	0.125
		T_5	782	20	796.5	20	0.13
		T_6	781.5	25	797	25	0.13
		T_7	779	27	796.5	25	0.145
	7	T_1	1065	7.2	1226	12.5	0.65
		T_2	1061	10	1219	17	0.65
		T_3	1061	18	1220	23	0.655
		T_4	1060.5	24	1220	38	0.67
		T_5	1060	30	1225	46	0.68
		T_6	1060	30.5	1228	52	0.695
		T_7	1057	31	1223	55	0.695
	8	T_1	1158	9.3	1155	9.3	0.01
		T_2	1156	15	1153	15	0.01
		T_3	1157	23	1154	23	0.008
		T_4	1155	40	1153	40	0.005
		T_5	1155	44	1154	44	0.003

$\epsilon_\infty = 2.356$

$T_1 = 295$ K $T_5 = 825$ K
$T_2 = 505$ K $T_6 = 860$ K
$T_3 = 620$ K $T_7 = 975$ K
$T_4 = 785$ K

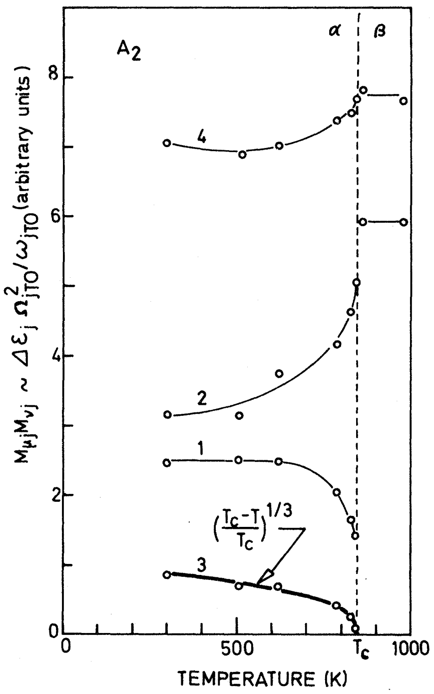

FIG. 3. Critical temperature dependence of dipolar moment components observed for the A_2 modes. Mode-3 data are fitted (heavy line) with a function of the form $[(T_c - T)/T_c]^\alpha$ with $\alpha = 1/3$. Small lines are only to guide eyes.

of the product of dipolar moment components

$$M_{\mu j}M_{\nu j} = (\hbar v/8\pi)\Delta\epsilon_j\Omega^2_{j\mathrm{TO}}/\omega_{j\mathrm{TO}} \tag{3}$$

than in terms of classical oscillator strength when it is analyzed as a function of temperature. $\omega_{j\mathrm{TO}}$ is the TO harmonic frequency. $M_{\mu j}M_{\nu j}$ deduced from the oscillator strength of the A_2 modes is plotted in Fig. 3 versus temperature. A function of the form $[(T_c - T)/T_c]^{1/3}$ correctly fits the mode-3 data. This function is the order parameter proposed by Höchli and Scott[5] based on critical fluctuation theory, but alternatively Dorner *et al.*[22] consider this function as the square of the order parameter and point out that the latter function or a formula derived from molecular field theory[23] fit their data equally well. The $M_{\mu j}M_{\nu j}$ function for the three other A_2 modes likewise critically behaves in the α phase at the approach of the phase transition. Inspection of Table II similarly shows that the polar character of modes $E^{(3)}$, $E^{(5)}$, and $E^{(8)}$ critically vanishes at the approach of the phase transition, whereas that of mode $E^{(4)}$ increases.

B. Frequencies

Perhaps the most striking effect concerning the temperature dependence of the infrared modes of quartz in the vicinity of the $\alpha-\beta$ phase transition is the behavior of the frequencies (Fig. 4). Critical softening *or hardening* are displayed in the α phase *and in the α phase only,* at the approach of the phase transition, particularly for the low-frequency modes ($\omega < 550$ cm^{-1}). This is somewhat surprising since normal modes alone are concerned.

Now the dipolar moments of A_2 modes are perpendicular to the resultant of the atomic displacements into the new equilibrium position occurring at the change of phase.[24] Consequently, contrary to the soft mode[2–5], A_2 modes should not be directly coupled to the order parameter.

The harmonic lattice force constants which govern the frequencies of the infrared modes in the α and β phases apparently derive from a single force field as confirmed by recent lattice dynamics calculations.[25] The frequencies should be renormalized to account for lattice thermal expansion and atom rearrangement effects which cause a frequency shift of the form

$$\delta\omega_j(T) = -\,\omega_j \int_0^T g_j(T)\,\alpha_V(T)\,dT\ , \tag{4}$$

where g_j is the mode Grüneisen parameter (MGP) and $\alpha_V(T)$ the volume thermal expansion coefficient. The change of volume of quartz $\Delta V(T)/V$ shown[26] in the upper part of Fig. 4, appears strikingly similar to the temperature dependence of the frequency shifts of most of the modes. Consequently in a first approach, we have assumed that (i) MGP is temperature independent so that Eq. (4) is rewritten

$$\delta\omega_j(T) = -\,\omega_j g_j \Delta V(T)/V \tag{5}$$

and (ii) purely anharmonic frequency shifts[27–29] can be neglected or positive and negative anharmonic contributions counterbalance each other.[30,31] Then Eq. (5) correctly fits the temperature dependence of a number of frequencies (Fig. 4). The adjustable parameter is the MGP only. MGP values found for the A_2 modes are $g_{1\mathrm{LO}} = -0.9$, $g_{2\mathrm{LO}} = 0.9$, $g_{3\mathrm{LO}} = 0.4$, and for the E modes $g_{3\mathrm{TO}} = -0.4$, $g_{3\mathrm{LO}} = -0.15$, $g_{4\mathrm{TO}} = 1.2$, $g_{4\mathrm{LO}} = 0.7$. A fit to other frequency shifts would require temperature-dependent MGP. Unfortunately, MGP data are unknown in quartz. Nevertheless values found in this rough approach are not unrealistic, since the macroscopic Grüneisen parameter of quartz calculated with the formula $g = \alpha_V V_M/\chi C_V$ is found equal to 0.7 at room temperature. Anyhow, measurement or calculation of MGP would be highly desirable, to confirm or invalidate the present provisional conclusion, particularly for the A_2 modes for which the effects are the most marked.

Otherwise, purely anharmonic frequency shifts almost certainly contribute to the observed frequencies although a balance between positive and negative contributions might occur incidentally and minimize the effect.[27–31] But in the present state of experimental data, whereas there exists support

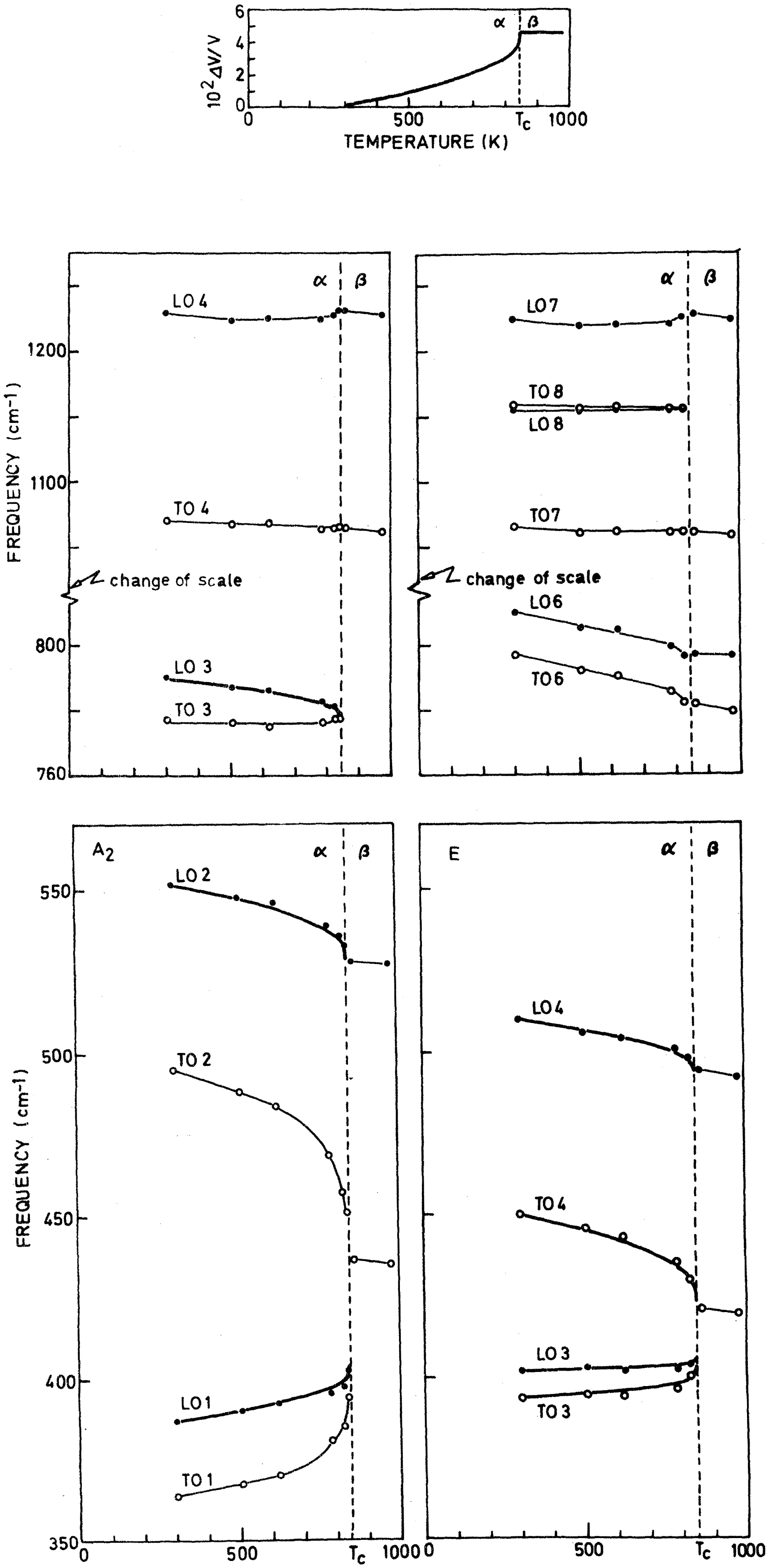

FIG. 4. Temperature dependence of the TO and LO frequencies of the A_2 and E modes in the α and β phases of quartz. Heavy lines are fits to the data with the aid of Eq. (5) by adjusting the mode Grüneisen parameter g_j only. The change of volume of quartz expressed in per cent vs temperature as taken from Ref. 26 is shown in the upper part of the figure. Small lines are guide to eyes.

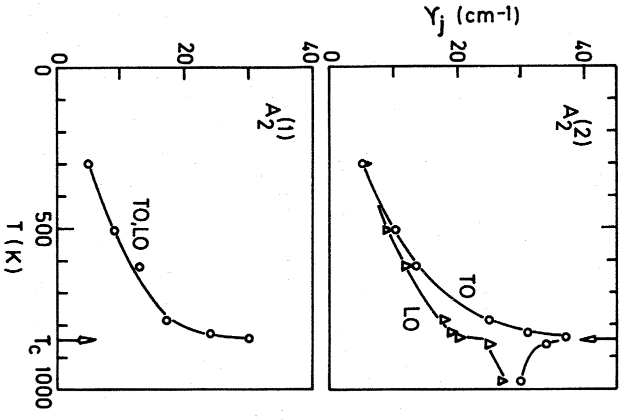

FIG. 5. Temperature dependence of damping of TO and LO low-frequency A_2 modes. Critical effects are observed in the vicinity of the transition temperature.

to a quasiharmonic explanation of the critical behavior observed presently due to the similarity to the lattice thermal expansion, conversely the assumption of an anharmonic origin of such unusual frequency shifts is speculative.

C. Damping

The dependence of damping on temperature (Tables I and II) is nearly linear in the range 300–700 K (see also Ref. 32) thus characteristic of cubic anharmonicity.[10,11,27,28] A critical increase of damping is observed at the approach of the transition. Damping of modes $A_2^{(1)}$ and $A_2^{(2)}$ are plotted in Fig. 5 vs temperature to illustrate this behavior. The mean number of phonons $N_s = [\exp(\hbar\omega_s/k_BT) - 1]^{-1}$ belonging to a soft branch[2,8] critically increases at the approach of the transition temperature, as a result of the critical decrease of the frequency ω_s. If a coupling of mode j to a soft branch s through anharmonic cubic potential is assumed (of course, the conservation laws imply the existence of a phonon of suitable frequency $\omega_{j\pm s} = \omega_j \pm \omega_s$ and suitable wave vector), then j mode damping is expected to diverge at the approach of T_c since perturbation theory[27] indicates that N_s enters the damping function in addition to all other N_i for phonons which satisfy the conservation laws.

IV. CONCLUDING REMARKS

Apart from degenerate E modes (labeled 5 and 8), an interesting aspect of the present results is the

TABLE III. A comparison of existing Raman and infrared data for the E-type modes at room temperature (all data in cm^{-1} unit).

	Raman data									Infrared data			
	Scott *et al.* (Ref. 14)	Shapiro *et al.* (Ref. 3)	Zubov *et al.* (Ref. 16)	Bates *et al.* (Ref. 6)	Tekippe *et al.* (Ref. 18)	She *et al.* (Ref. 17)		Biraud-Laval (Ref. 19)		Spitzer (Ref. 13) Merten (Ref. 15)*		Present work	
	Ω_j	Ω_j	Ω_j	Ω_j	Ω_j	Ω_j	γ_j	Ω_j	γ_j	Ω_j	γ_j	Ω_j	γ_j
(TO, LO)1	128	128	128	128	127.5	127.6	4.3	128	7 ± 0.5	···	···	···	···
(TO, LO)2	265	264	267	265	263	264.6	4	265	4.5 ± 0.5	···	···	···	···
TO3	394	394	392	394	392.7	394	2 ± 1	395	3 ± 0.5	394	2.75	393.5	2.8
LO3	401	403	402	401	400.2	403	2.4 ± 1.3	···	···	402.7*	···	402	2.8
TO4	450	452	···	450	450	449	2.5 ± 0.7	452	7 ± 0.5	450	4	450	4.5
LO4	509	508	···	509	···	508	2.1 ± 1.6	···	···	509.8*	···	510	4.1
TO5	697	698	696	697	695	696	···	702	6 ± 0.5	697	8	695	(13)
LO5										699*	···	697.6	(13)
TO6	795	798	795	795	795.6	796	6.5 ± 1.3	799	10 ± 1	797	7.2	797	6.9
LO6	807	811	805	807	804.9	809	6.3 ± 0.8	···	···	809.7*	···	810	6.9
TO7	1072	1067	1061	1072	1064.1	1068	4.3 ± 2.4	1072	7 ± 1	1072	7.6	1065	7.2
LO7	1231-5	1233	1228	1231-5	1231.1	1230	7.9 ± 2.4	···	···	1237*	···	1226	12.5
TO8	1162	1161	1159	1162	1159.9	1159	11 ± 2.2	···	···	1163	7	1158	9.3
LO8										1160*	···	1155	9.3

close similarity between the frequency behaviors of A_2 and E modes as a function of temperature when a correspondence based on their position in the spectral range is established (Fig. 4), though critical behaviors are less marked for E modes. The same similarity is to be noted for the oscillator strengths of A_2 and E modes apart from the $E^{(6)}$ mode which remains infrared active in the β phase contrary to the corresponding $A_2^{(3)}$ mode. A comparison of infrared reflectivity spectra displays these similarities also (Figs. 1 and 2). Roughly speaking, quartz might be qualified as quasiisotropic in term of infrared properties. This is due to the fact that infrared modes can be considered as deriving from the fundamental stretching (high-frequency) and bending (low-frequency) modes of the SiO_4 tetrahedron. The same situation holds for the internal modes of silicates as well.[33]

Note added in proof. J. F. Asell and M. Nicol [J. Chem. Phys. 49, 5395 (1968)] have suggested previously that "the temperature and pressure dependence of phonon frequencies in α-quartz simply reflect their dependence on the separation between atoms in a way that could be represented as a volume dependence," which is nothing else than the present tentative conclusion. Within the Asell and Nicol measurement precision, the 393-, 402-, 1065-, 1155-, and 1226-cm^{-1} E-type modes are pressure independent and they are consistently found to be nearly independent of temperature in the vicinity of room temperature (Table II). MGP values deduced from pressure measurements for the 695-, 797-, and 810-cm^{-1} modes, viz., 0.45, 0.4, and 0.4, respectively, are to be compared with 0.6, 0.45, and 0.4 as obtained by fit of Eq. (5) to the present data. The quasiharmonic explanation of the frequency behaviors observed in this paper is thus verified for the limited number of modes for which very-high-pressure data are available. Fries and Claus (J. Raman Spectrosc. 1, 71) have reported the Raman frequency of two LO modes of the E_1 type which were not observed by Bates and Quist (Ref. 6), in the β-phase. Both frequencies and the present results agree perfectly.

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