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High Pressure Far Infrared Spectroscopy of Ionic Solids

R. P. LOWNDES

***Abstract*—A high pressure far infrared cell operating to truly hydrostatic pressures of 8 kbar is described and used to determine the anharmonic self-energies associated with the $q \approx 0$ transverse optic modes of ionic solids.**

I. INTRODUCTION

HIGH pressure far infrared studies can provide crucial information in many research areas including studies of anharmonicity in solids, studies of phase and ferroelectric transitions, and studies of defects in solids. If meaningful information is to be obtained from such researches, however, then it is clear that the high pressures must be applied hydrostatically. Unfortunately, far infrared studies under truly hydrostatic pressures are difficult primarily because of the lack of a readily available window material which satisfies the competing demands of strength and transmissivity in the far infrared. To date, much of the very limited far infrared high pressure research has been confined to work achieved with the opposed diamond anvil system [1]. However, reliable measurements are difficult to perform with this instrument due to the inherent difficulties of eliminating the pressure gradients generated across the opposed anvil faces and of accurately determining the system operating pressure. The consequences of these problems are that it is difficult to precisely determine the pressure dependence of mode eigenfrequencies and it is virtually impossible to reliably measure their spectral linewidths as a function of pressure using the diamond anvil system. In this paper we describe a high pressure far infrared cell which goes some way to solving these problems and which allows far infrared studies in the spectral range below 120 cm^{-1} for hydrostatic pressures up to 8 kbar. We describe investigations using this cell to determine the mode Gruneisen constants and the pressure dependence of the inverse lifetimes of the $q \approx 0$ transverse optic modes of RbI, CsI, and TlCl and use these measurements to investigate the complex anharmonic self-energy of these modes.

II. HIGH PRESSURE FAR INFRARED CELL

The high pressure far infrared cell used in these investigations is illustrated in Fig. 1. The cell body, window mounts, and retaining closures were machined from 4340 alloy steel and then heat treated to a hardness of RC 50 giving a yield strength of 14 kbar. The critical bores and surfaces of the cell and its components were ground and honed to size after the hardening process. Fully assembled, the cell had an effective speed of $f2.4$.

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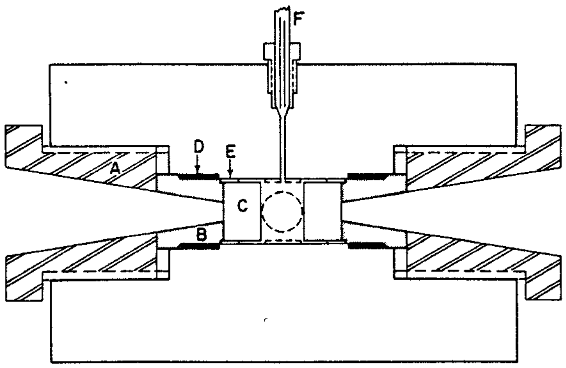


Fig. 1. The far infrared high pressure cell. *A*, retaining closure; *B*, window mount; *C*, window; *D*, packing; *E*, window retaining ring; *F*, gas input line.

TABLE I

Window Material	Crystal Quartz				Fused Quartz
Window Thickness (mm)	3.1	6.4	6.4	12.5	12.5
Pressure Transmission Media	Ar	Ar	N_2	Ar	Ar
Maximum Operating Frequency (cm^{-1})	120	95	45	70	65
Maximum Sustainable Pressure (kbar)	3	6	6	> 8	7

Note: Summary of typical spectral and high pressure operating data for different window materials and pressure transmission media used in the high pressure cell. The data refer to use of the cell in conjunction with an RIIC (London) FS 720 Fourier spectrophotomer and a Unicam (Cambridge) Golay detector. The maximum operating frequency refers to a frequency above which only signal to noise ratios of <40 would be achieved. The maximum sustainable pressure refers to a pressure to which, and at which, we have routinely worked.

The window mounts used in the cell gave a supported to unsupported area ratio of about 3 with an unsupported port diameter of 5 mm. The window high pressure seal was achieved by lapping and polishing the mating surfaces of the window and its mount to be flat and parallel to better than 500 Å. The windows were prevented from sliding off their mounts by brass retaining rings attached to the window mounts. The window mount high pressure seal was achieved using a stainless-steel brass Teflon packing assembly.

In choosing both the cell windows and the pressure transmission medium, care must be used to avoid materials which have characteristic electromagnetic resonances in the spectral region under investigation. The choice of materials available for both windows and pressure transmission media for far infrared service is extremely restricted. As far as windows are concerned, the most useful materials are diamond, sapphire, and crystal and fused quartz. Diamond, of course, has both the strength and transmissivity required of a far infrared high pressure window, but for the present cell, which used windows 1.8 cm in diameter, such windows are not available on economic grounds. Sapphire has sufficient strength for high pressure service but at room temperature gives a strong attenuation throughout the far infrared region: at low temperatures this multiphonon absorption disappears, however, and sapphire becomes a viable high pressure far infrared window at such temperatures. For room temperature service, therefore, we are left with crystal and fused quartz. Both of these materials are significantly weaker than both sapphire and diamond and, furthermore, they both have some lattice resonances in the far infrared; nevertheless, thick crystals of these materials can be used for high pressure service below about 120 cm^{-1}. The windows used in the present experiments were *z* cut crystal quartz blanks. Fused quartz has also been used but it tends to fracture at somewhat lower pressures than crystal quartz.

The choice of pressure transmission media for the far infrared is also very limited. Most organic oils conventionally used in high pressure research exhibit characteristic spectral resonances in the far infrared and so are unsuitable. Many gases exhibit their associated molecular spectra in the far infrared and, under pressure, collision induced absorption becomes an increasing problem in many gases. The inert gases, however, can be used for high pressure service in the far infrared. In general, we have used argon gas in the present high pressure experiments, primarily because of its lower leak rate over that for helium for a given pressure system.

Table I itemizes the various operating spectral and high pressure ranges for some different window materials and pressure transmission media used in the high pressure cell and determined using a Michelson–Fourier transform spectrophotometer (RIIC FS 720) and a Golay detector.

III. PRESSURE DEPENDENCE OF LATTICE RESONANCES OF IONIC SOLIDS

Fig. 2 illustrates the pressure dependence of the spectral profile associated with the $q \approx 0$ transverse optic mode of RbI (in its NaCl phase) at room temperature. The figure reveals that the application of pressure has little consequence for the spectral profile itself but that it does lead to a continuous shift to higher frequencies with increasing

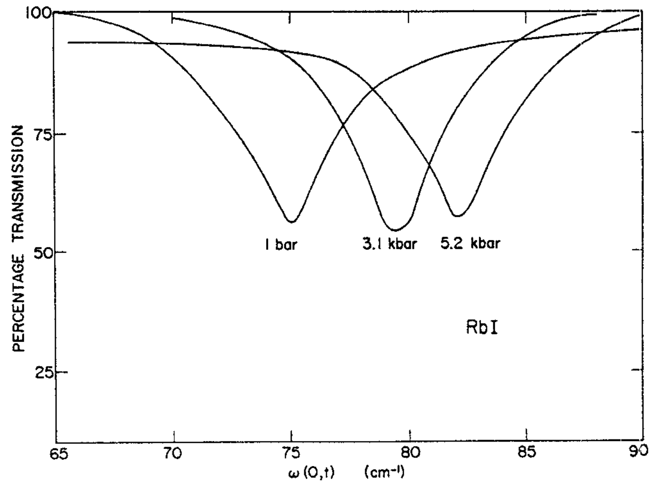
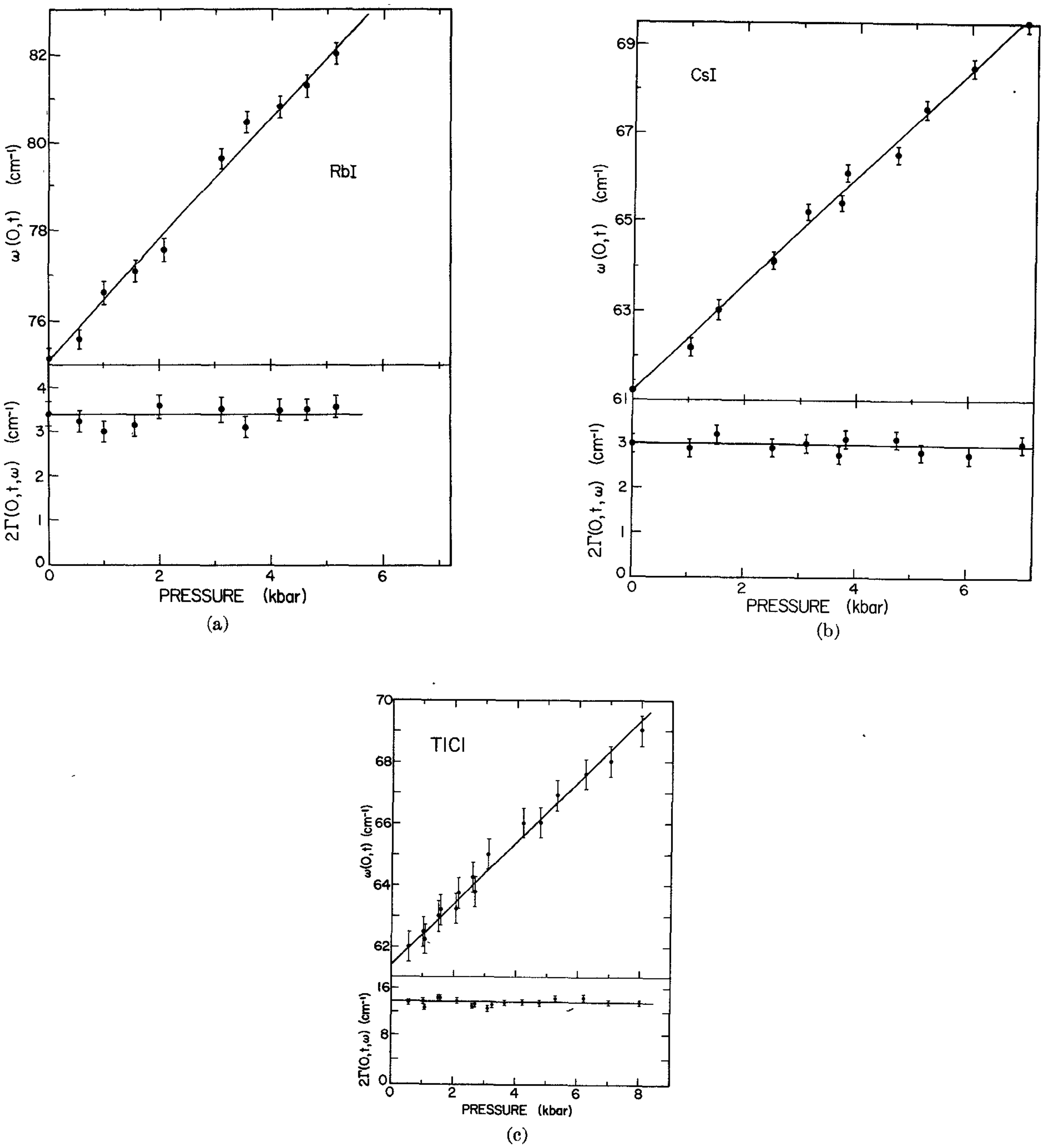


Fig. 2. Pressure dependence of the transmission spectral profile of the $q \approx 0$ transverse optic phonon of RbI (in its NaCl phase).



(a)

(b)

(c)

Fig. 3. Pressure dependence of $\omega(0,t)$ and $\Gamma(0,t,\omega)$ for (a) RbI, (b) CsI, and (c) TlCl.

pressure of the profile as a whole; we find such behavior to be common for all three materials. Fig. 3(a)–(c) displays the detailed pressure dependence of the frequency $\omega(0,t)$ and inverse lifetime $\Gamma(0,t,\omega)$ of the transverse optic mode for the three materials. The figures reveal that, within the pressure range covered, the $\omega(0,t)$ increase linearly with increasing pressure; such behavior yields mode Gruneisen constants of 2.27 ± 0.11, 2.53 ± 0.10, and 3.73 ± 0.34 for RbI, CsI, and TlCl, respectively. The $\Gamma(0,t,\omega)$, however, appear to be largely invariant to changes of pressure, and least squares fits to the data confirm that no significant trend is revealed for the volume dependence of $\Gamma(0,t,\omega)$ up to 8 kbar.

IV. DISCUSSION OF RESULTS

The temperature dependence of each phonon frequency in the Brillouin zone stems from the anharmonic terms in the lattice potential energy in two separate ways. First, at each temperature T, the thermal expansion of the crystal creates a shift $\Delta^E(0,t)$ of each phonon frequency from the harmonic normal mode value to the quasi-harmonic frequency $\omega^E(\boldsymbol{q},j)$. Second, the anharmonic terms of the lattice potential energy permit a coupling between different normal modes which change the phonon energies and give them a finite lifetime. At a temperature T and an applied frequency Ω, each of the quasi-harmonic frequencies suffers a complex self-energy shift $D(\boldsymbol{q},j,\Omega)$

given by [2], [3]:

$$D(\boldsymbol{q},j,\Omega) = \Delta_T{}^A(\boldsymbol{q},j,\Omega) + i\Gamma(\boldsymbol{q},j,\Omega) \tag{1}$$

the real part of which shifts the frequency from $\omega^E(\boldsymbol{q},j)$ to the quasi-normal frequency $\omega(\boldsymbol{q},j)$, which is, to a good approximation, the solution for Ω of

$$\Omega^2 = \omega^E(\boldsymbol{q},j)^2 + 2\omega^E(\boldsymbol{q},j)\Delta_T{}^A(\boldsymbol{q},j,\omega) = \omega(\boldsymbol{q},j)^2 \tag{2}$$

and the imaginary part is the reciprocal of the lifetime for the phonon state. In this paper we shall be concerned only with the $q \approx 0$ transverse optic mode which will be designated by $(0,t)$. Low order perturbation calculations to second order in cubic and quartic anharmonicity yield $\Delta_T{}^A(0,t,\omega)$ to be [4]

$$\Delta_T{}^A(0,t,\omega) = \Delta^{(4)}(0,t) - \Delta^{(6)}(0,t,\omega) - \Delta^{(8)}(0,t) - \Delta^{(8)}(0,t,\omega) \tag{3}$$

where $\Delta^{(4)}(0,t)$ is a frequency independent first order quartic term, $\Delta^{(6)}(0,t,\omega)$ is a frequency dependent second order cubic contribution, $\Delta^{(8)}(0,t)$ is a frequency independent second order quartic contribution, and $\Delta^{(8)}(0,t,\omega)$ is a frequency dependent second order quartic term. These various contributions involve complex lattice summations containing the Fourier transformed anharmonic force constants and the phonon population factors. In the same manner $\Gamma(0,t,\omega)$ is given by [4]

$$\Gamma(0,t,\omega) = \Gamma^{(6)}(0,t,\omega) + \Gamma^{(8)}(0,t,\omega). \tag{4}$$

Since the probability for the coupling between the normal modes depends on the phonon occupation numbers, the self-energies therefore allow the phonon energies to be temperature dependent even under constant volume. By measuring both the isobaric temperature dependence and the isothermal pressure dependence of the $q \approx 0$ transverse optic phonons in RbI, CsI, and TlCl, therefore, we have been able to separately determine both $\Delta^E(0,t)$ and $\Delta_T{}^A(0,t,\Omega)$ for these materials.

If $\Delta\omega_T(0,t)]_V$ is defined as the change in $\omega(0,t)$ on raising the temperature from 0 to T isochorically at the volume that the crystal has at 0 K and (essentially) zero pressure, then it can be determined from

$$\Delta\omega_T(0,t)]_V = \Delta\omega_T(0,t)]_P + \Delta\omega(0,t)]_T \tag{5}$$

where $\Delta\omega_T(0,t)]_P$ is the change in $\omega(0,t)$ on raising the temperature from 0 to T isobarically at (essentially) zero pressure and $\Delta\omega(0,t)]_T$ is the change in $\omega(0,t)$ on raising the pressure isothermally at a temperature T so as to restore the volume of the crystal to that which it has at 0 K and (essentially) zero pressure.

The isobaric temperature dependence of $\omega(0,t)$ for the three materials investigated here has been measured previously at zero pressure for the range 4–290 K [5], thus leading to a determination of $\Delta\omega_T(0,t)]_P$. Values of $\Delta\omega(0,t)]_T$ at 290 K are determined directly from the pressure dependence of $\omega(0,t)$ reported here, since the pressure required to reduce the crystal volume to that which it was at 0 K is in each case well within the pressure range covered in these experiments. As has been discussed elsewhere [6] there are reasonable grounds for believing that the quantity

$$\frac{V}{\omega(0,t)}\left(\frac{\partial\omega(0,t)}{\partial V}\right)_T$$

should not be very temperature dependent. If this is assumed to be true, then $\Delta\omega(0,t)]_T$ and hence $\Delta\omega_T(0,t)]_V$ can be determined for the temperature range 4–290 K.

Providing the mode self-energies are not too large compared to the harmonic frequencies, it is readily shown that [7]

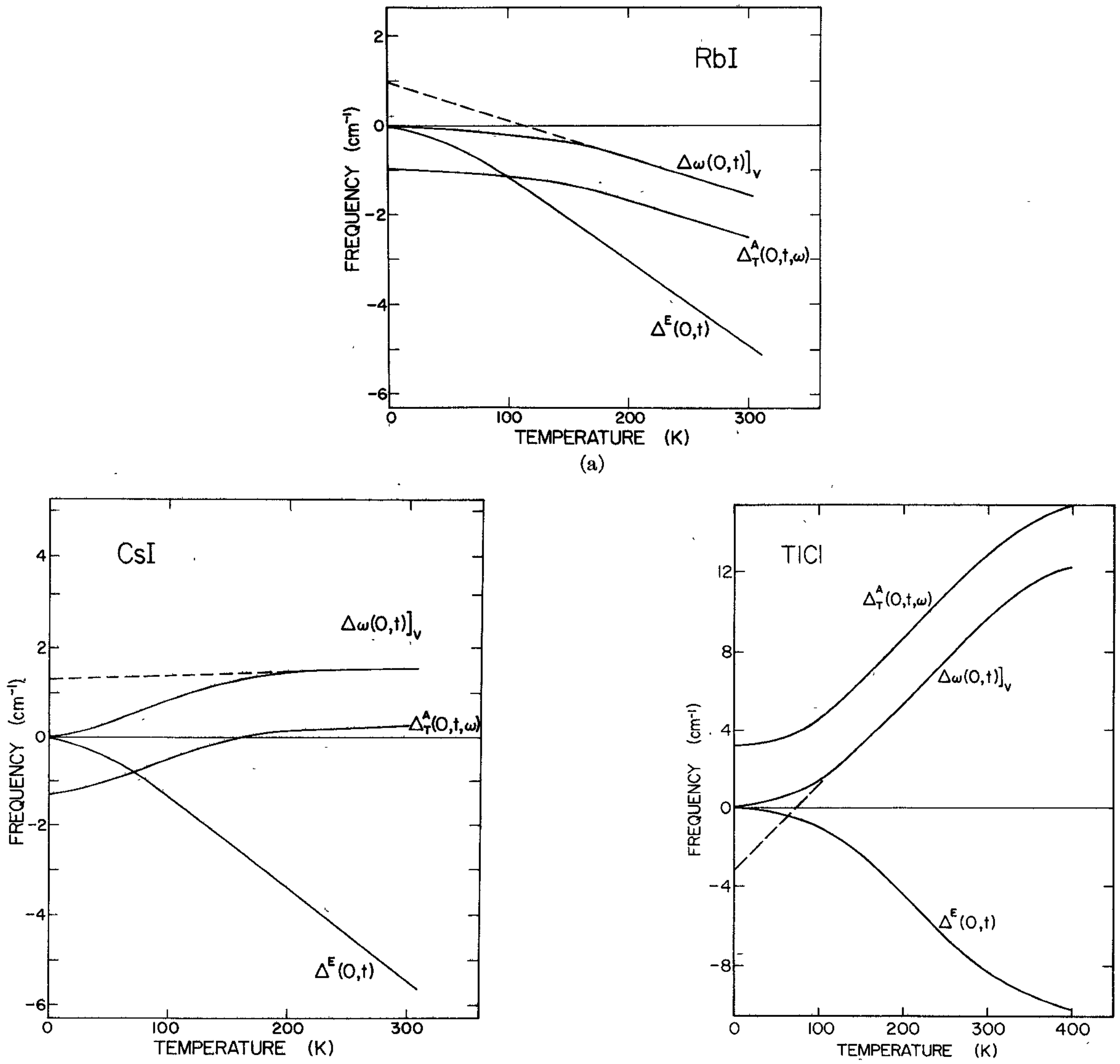
$$\Delta\omega(0,t)]_T = -\Delta^E(0,t) \tag{6}$$

and

$$\Delta\omega_T(0,t)]_V \simeq [\Delta_T{}^A(0,t,\omega) - \Delta_0{}^A(0,t,\omega')]. \tag{7}$$

$\Delta\omega(0,t)]_T$ therefore determines the frequency shift due to the thermal strain and $\Delta\omega_T(0,t)]_V$ gives a measure of the change in $\Delta_T{}^A(0,t,\omega)$ at temperature T from the value which it has at 0 K. $\Delta_0{}^A(0,t,\omega)$ is not necessarily small or zero but an estimate can be made of its magnitude. The theoretical description [2], [3] of $\Delta_T{}^A(0,t,\omega)$ suggests that at temperatures above the characteristic Debye temperature (but not too high) the $\Delta_T{}^A(0,t,\omega)$ should have a linear temperature dependence. Examination of Fig. 4 reveals that such a linearity in $\Delta\omega_T(0,t)]_V$, and hence in $\Delta_T{}^A(0,t,\omega)$, does exist at higher temperatures. Extrapolations to $T = 0$ from these linear parts of $\Delta\omega_T(0,t)]_V$ (see Fig. 4) have therefore given an intercept which provides a reasonable estimate of $-\Delta_T{}^A(0,t,\omega')$. Fig. 4 shows the temperature dependence of $\Delta^E(0,t)$ and $\Delta_T{}^A(0,t,\omega)$ determined for the three compounds. For RbI and CsI at low temperatures $\Delta_T{}^A(0,t,\omega)$ is a negative quantity. As the temperature is increased, $\Delta_T{}^A(0,t,\omega)$ for RbI remains negative, increasing in magnitude. Even at room temperature, however, $\Delta_T{}^A(0,t,\omega)$ is only about half the magnitude of $\Delta^E(0,t)$, although it is of the same sign. For RbI, therefore, both $\Delta^E(0,t)$ and $\Delta_T{}^A(0,t,\omega)$ cause $\omega(0,t)$ to decrease with increasing temperature. For CsI a somewhat different behavior for $\Delta_T{}^A(0,t,\omega)$ is observed. In this case $\Delta_T{}^A(0,t,\omega)$ decreases in magnitude as the temperature is increased from $T = 0$ K until at 160 K it changes sign becoming a positive quantity. At still higher temperatures $\Delta_T{}^A(0,t,\omega)$ remains a small quantity varying only slowly with temperature. It is clear from (3) that, to second order in perturbation theory, this positive sign found for $\Delta_T{}^A(0,t,\omega)$ arises from the dominance of the first order quartic contribution to the anharmonic self-energy. Again, however, $\Delta^E(0,t)$ provides the overall dominant contribution to the shift of $\omega(0,t)$ with temperature, although now $\Delta^E(0,t)$ and $\Delta_T{}^A(0,t,\omega)$ are competing terms.

For TlCl, $\Delta_T{}^A(0,t,\omega)$ is found to be a positive quantity at all temperatures in the range investigated. As the temperature is increased $\Delta_T{}^A(0,t,\omega)$ also increases rapidly, with $\Delta^A(0,t,\omega)$ now dominating the thermal strain con-



(a)

(b)

(c)

Fig. 4. Temperature dependence of $\Delta\omega(0, t)]_V$, $\Delta_T{}^A(0, t, \omega)$, and $\Delta^E(0, t)$ for (a) RbI, (b) CsI, and (c) TlCl.

tribution $\Delta^E(0,t)$. Clearly this dominance is caused by a strong first order quartic contribution to the anharmonic self-energy and it is thus this quantity which causes the transverse optic mode in TlCl to exhibit a weak soft mode behavior [7].

Finally we discuss the apparent volume independence found experimentally for $\Gamma(0,t,\omega)$. An analysis of the detailed expression for $\Gamma(0,t,\omega)$ described by (4) shows that any volume dependence of $\Gamma(0,t,\omega)$ can come only from the volume dependence of the Fourier transformed anharmonic force constants and indirectly from any pressure dependence of the lattice frequencies contained in the thermal population factors. Numerical analyses of these effects, of the type described by Rastogi *et al.* [8], reveal that both effects would cause only about a 1-percent per kilobar decrease in $\Gamma(0,t,\omega)$, which is well in agreement with our experimental findings (within their experimental error).

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