Pressure dependence of the Raman scattering by copper halides*

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We report Raman scattering in CuI, CuBr, and CuCl at 40, 100, and 295 K under hydrostatic pressures from 1 to 7 kbar. The TO- and LO-mode Grüneisen parameters are determined for cases in which these modes are directly observed experimentally. By combining the experimental pressure dependence of the phonon frequencies with the experimental temperature dependence one can separate the anharmonic contributions into volume effects and multiphonon effects. In most cases the major contribution to the isobaric temperature dependence of the phonon frequencies in these crystals is the temperature dependence of the anharmonic coupling of the phonons. The logarithmic derivative of the Szigeti effective charge is calculated from mode Grüneisen parameters; in CuBr at 40 K the value of this derivative is anomalous. A new design for sapphire windows for use in pressure cells is described.

I. INTRODUCTION

The lattice dynamics of the cuprous halides have been studied extensively.[1-7] Much of the recent interest results from the fact that these materials exhibit large anharmonicity; CuBr and CuCl undergo negative thermal expansion at low temperatures.[8,9] Although common to many zinc-blende crystals, the negative thermal expansion in CuCl is larger than in any other crystal. It has been correlated to the negative mode Grüneisen parameters of the long-wavelength transverse-acoustic phonons.[4(b)] Further evidence of anharmonicity can be seen in the Raman spectra of these materials.[6,10,11] At temperatures as low as 200 K the observed peaks are very broad, indicating large anharmonic coupling of the phonons.

Potts *et al.* have reported extensive studies of the zone-center phonon frequencies as a function of temperature for CuI, CuBr, and CuCl.[6] The LO phonon in CuBr and CuCl decreased in frequency as the temperature was lowered below 70 and 100 K, respectively. They suggested that this may reflect the negative thermal expansion of these crystals. On the other hand, multiphonon effects may account for this effect. Therefore it is clearly of interest to separate the temperature dependence of the phonon frequencies into a part due to volume dependence and a part due to multiphonon effects.

Such a determination can be made by combining the temperature dependence with the hydrostatic pressure dependence of the phonon frequencies.[12-15] We, therefore, report here measurements of the Raman scattering in CuI, CuBr, and CuCl at several temperatures from pressures of 1–7 kbar. In addition to the separation described above, we determine the mode Grüneisen parameters of the TO and LO phonons.

II. EXPERIMENTAL CONSIDERATIONS

CuI, CuBr, and CuCl have the zinc-blende structure and should thus show zone-center TO and LO phonons in their Raman spectra. To observe both modes in one spectrum rectangular samples were cut from single crystals with [110] and [001] surfaces. The incident beam propagated along [110] and the scattered light was collected along [001]. As the beam is depolarized by the sapphire windows of the pressure cell, both TO and LO modes are present in each spectrum.

Pressure was generated with a conventional system (hydraulic pump and intensifier) with helium being the pressure transmitting medium. Helium allows low-temperature measurements and also provides excellent thermal conductivity. Thus we were able to use relatively high laser power (300 to 500 mW) without excessive sample heating. The high-pressure tubing was $\frac{1}{16}$-in.-o.d. $\times$ 0.010-in.-i.d. SS 316 stainless steel. This is very flexible, makes assembly of the system easier and prevents misalignment of the optical system during cooling. In addition, it is safer than thicker tubing because the energy stored in the tube is small. It does have the disadvantage that pressure in the cell is built up relatively slowly. Therefore this tubing cannot be used with cells in which the sapphires must quickly push against their seals with large forces.[16]

Our pressure cell features a new design which allows the sapphires to be stressed before cell assembly. The sapphires are mounted in maraging steel plugs with a screw cap which applies the stress; the assembly is shown schematically in Fig. 1. The sealings for the sapphires are aluminum-gold-aluminum packings, each 0.2 mm thick and placed between the sapphire and the flat

wall of the plug. The screw cap is then tightened, prestressing the sapphire. This procedure reduces the importance of highly polished surfaces of contact of sapphire and plug. In addition, the prestress provides a seal at very low pressures for the initial run. After the high pressures have been applied to the plug with helium gas the packings have extruded and the screw cap is no longer providing a stress; thus we are not able to return to very low pressures (less than approximately 1.5 kbar at 40 K). With this design it is essential that the sapphires are Verneuil-growth type. These have more impurities than the Czochralski-growth type and are more resistant to cleavage.

The plugs themselves are sealed against the cell walls conventionally.[16,17] Packings for this seal are also shown schematically in Fig. 1.

The pressure cell is a four window design, also made from maraging steel. We use three optical windows. The sample holder has no connection with the window plugs, preventing misalignment under pressure. Polarizing sheets may be placed inside the cell to permit polarized measurements under pressure. The pressure cell is mounted on a cold finger in a conventional liquid-helium optical cryostat. At low temperatures and high pressures helium is solid, and therefore the cell was attached with the pressure tubing at the side of the cell opposite the cold finger. This ensures that the helium freezes at constant pressure rather than at constant volume and simplifies the pressure determination inside the cell. We follow normal procedure and pressurize the cell before cooling to freeze in strains in the metal. This minimizes the possibility of the cell exploding. We are able to change from one pressure to another (staying above ~2 kbar) at 100 K without incident. The pressure is measured to ±20 psi with a Harwood manganin cell. The temperature is measured with carbon resistors and a thermocouple outside the cell and is regulated to ±2 K with an Artronix controller. We estimate that the sample is only a few degrees warmer than our measured temperatures.
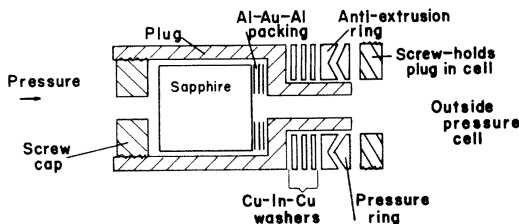

FIG. 1. Cross-section schematic of sapphire window assembly.

III. RESULTS

Figures 2, 3, and 4 show the Raman spectra of CuI, CurBr, and CuCl at low and high hydrostatic pressures at 40, 100, and 295 K. The frequency shifts of peaks in the spectra of CuI and CuBr are seen clearly. The TO and LO phonons in CuI (~135 and ~150 cm^{-1} at 40 K) are seen as symmetric peaks at 40 and 100 K throughout the pressure range shown. The TO phonon of CuBr (~135 cm^{-1} at 40 K) behaves in a similar manner. The LO phonon of CuBr produces an asymmetric peak (~170 cm^{-1} at 40 K); at 100 K its asymmetry clearly decreases with pressure. The region of the TO phonon in CuCl (~140–180 cm^{-1} at 40 K) is clearly anomalous. A detailed description of the experimental results at 40 K and a theoretical model reproducing the spectra are described elsewhere.[7] The LO phonon of CuCl (~205 cm^{-1} at 40 K) is seen as a symmetric peak at 40 and 100 K.

The 295-K data for all three materials show broad structure. In the case of CuI the two largest peaks correspond to the TO and LO phonons. For CuBr the largest peak consists of contributions from both the TO phonon and a two-phonon difference band; the smaller peak corresponds to LO phonon scattering. Finally, CuCl indicates four peaks, previously labeled[11] from low to high frequency as α, β, γ, and δ. The peaks β, γ, and δ correspond to the three peaks observed in the 40 and 100 K spectra.

We have determined the pressure dependence of the frequencies of the phonons described above. Typical results are shown in Fig. 5 for data obtained at 100 K. The straight lines are least squares fits to the frequency versus pressure data and provide the information necessary to calculate the mode Grüneisen parameter, γ:

$$\gamma_i = -\left(\frac{\partial \ln \omega_i}{\partial \ln V}\right)_T = \frac{1}{\kappa_T}\left(\frac{\partial \ln \omega_i}{\partial P}\right)_T \qquad (1)$$

where $\kappa_T = -(1/V)(\partial V/\partial P)_T$ is the isothermal compressibility. Values of γ_i are shown in Table I. Also shown is the value of κ_T used to determine γ_i and β, the volume thermal expansion coefficient, which is used in the calculation of κ_T and the volume contribution to the isobaric temperature dependence of the mode frequency. Values of the pressure derivatives, with standard deviations, are tabulated in Table III (along with temperature derivatives). The isothermal compressibilities are determined from the isothermal bulk moduli, B_T: $\kappa_T = 1/B_T$. B_T is determined from the adiabatic bulk moduli B_S, which is, in turn, determined from elastic constants (c_{11} and c_{12}) using the relations

FIG. 2. Raman spectra of CuI at low and high pressure at 40, 100, and 295 K.
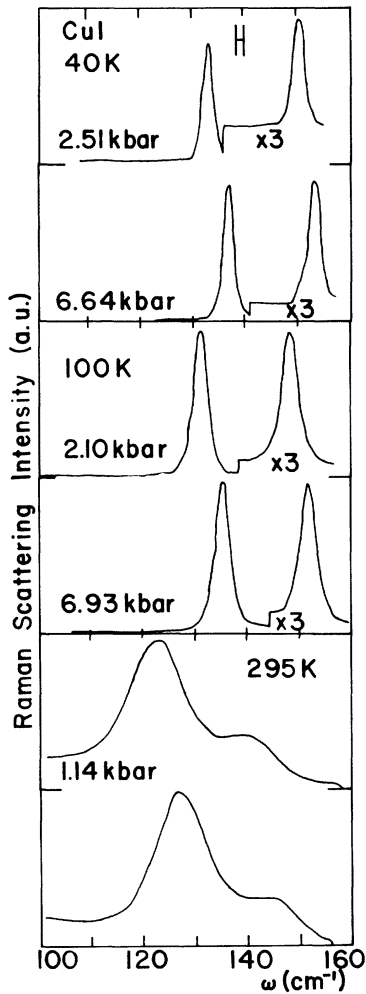

FIG. 3. Raman spectra of CuBr at low and high pressure at 40, 100, and 295 K.

$$B_S = \tfrac{1}{3}(c_{11} + 2c_{12}) \qquad (2)$$

and

$$B_T = B_S/(1+D) , \qquad (3)$$

where

$$D = B_S \, Tv\beta^2/c_p ,$$

in which v is the specific volume, c_p is the specific heat per mole at constant pressure, T is the temperature, and $\beta = (1/V)(\partial V/\partial T)_p$ is the volume thermal-expansion coefficient. D is much less than 1, so that the difference between B_T and B_S is from 1.2% to 2.5%. The elastic constants themselves change $\sim 5\%$ with pressure (0–7 kbar). We used the 1-bar values of the elastic constants.

The β and γ peaks in the spectra of CuCl may not be simply interpreted as corresponding to a single phonon.[7] For completeness, however, in Table

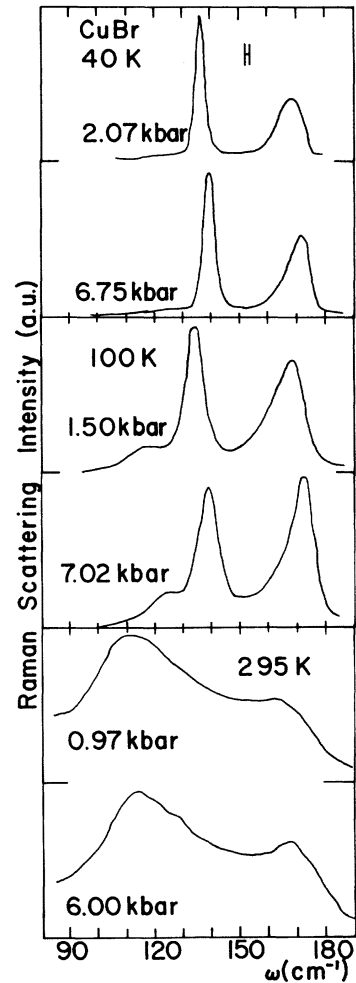II we present their pressure dependence along with that of the α peak.

IV. DISCUSSION

We consider first the values of γ_i themselves. In all three materials at all temperature measured $\gamma_{TO} > \gamma_{LO}$. This is the normal behavior for zinc-blende materials and is in agreement with pressure measurements in other materials.[21,22] That is to say increased pressure causes a decrease of the TO-LO splitting, which means a decrease of the effective charge; this point will be discussed quantitatively below. It can also be seen that these mode Grüneisen parameters show interesting temperature dependences. Because of the larger errors in the 295-K values of γ_i we consider only the 40 and 100 K values. γ_{TO} and γ_{LO} of CuI are, respectively, very nearly the same at 40 and 100 K. This
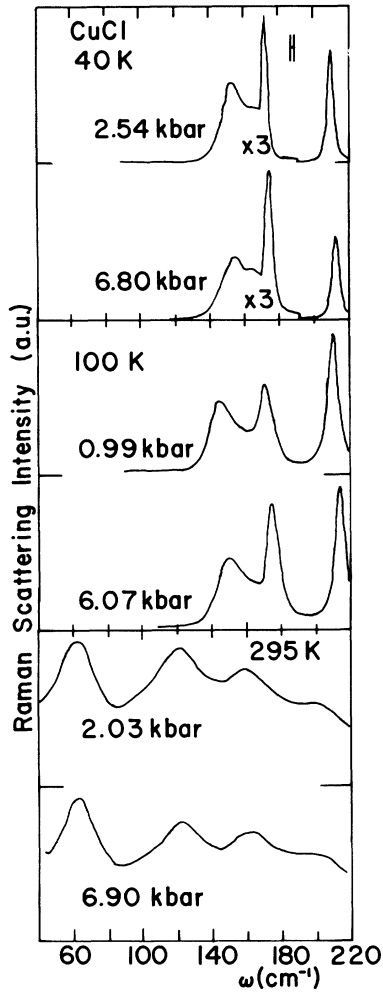
FIG. 4. Raman spectra of CuCl at low and high pressure at 40, 100, and 295 K.

FIG. 5. Phonon frequencies vs pressure of CuI, CuBr, and CuCl at 100 K.

is also the case for γ_{LO} of CuBr although the LO peak in CuBr is asymmetric, perhaps indicating a coupling to other modes or excitations.

γ_{TO} of CuBr, however, increases by 25% from 40 to 100 K. In addition, at 100 K it is much larger than γ_{TO} in CuI. γ_{LO} in CuCl also increases from 40 to 100 K. At 100 K, γ_{LO} is similar in CuI, CuBr, and CuCl while at 40 K, γ_{LO} of CuCl is significantly smaller than γ_{LO} of CuI or CuBr. These temperature effects in the mode Grüneisen parameters are not now understood.

We turn now to a comparison of the temperature and pressure dependences of the phonon frequencies. Treating the frequency as a function of volume V and temperature yields[14]

$$\Delta\omega_i = \left(\frac{\partial\omega_i}{\partial T}\right)_V \Delta T + \left(\frac{\partial\omega_i}{\partial V}\right)_T \Delta V. \tag{4}$$
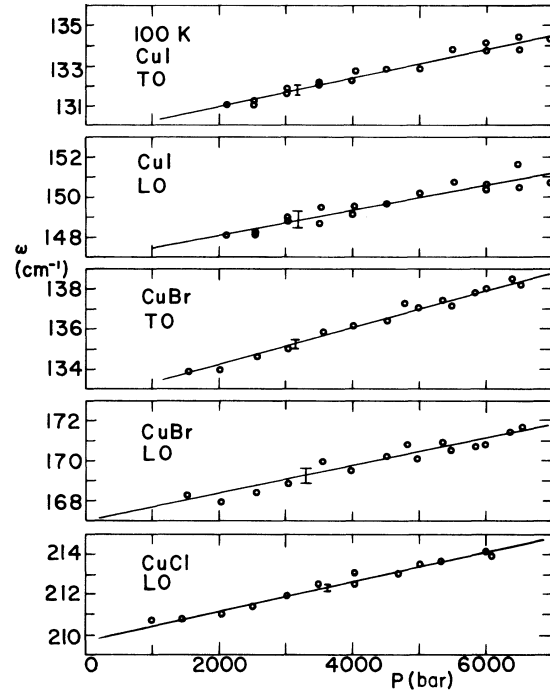
Taking the exact differentials at constant pressure and dividing by ΔT_p and ω_i results in

$$\left(\frac{\partial\ln\omega_i}{\partial T}\right)_P = \left(\frac{\partial\ln V}{\partial T}\right)_P\left(\frac{\partial\ln\omega_i}{\partial\ln V}\right)_T + \left(\frac{\partial\ln\omega_i}{\partial T}\right)_V$$

$$= -\frac{\beta}{\kappa_T}\left(\frac{\partial\ln\omega_i}{\partial P}\right)_T + \left(\frac{\partial\ln\omega_i}{\partial T}\right)_V \tag{5}$$

TABLE I. Mode Grüneisen parameters, isothermal compressibilities, and volume thermal expansion coefficients. The isothermal compressibilities have been determined from elastic constant data (Refs. 4 and 18). The volume thermal expansion coefficients have been determined from data of Schaake (Ref. 9) and Barron et al. (Ref. 8) (40 K CuCl only).

	γ_{TO}	γ_{LO}	κ_T (10^{-3}/kbar)	β (10^{-5}/K)
40 K:				
CuI	2.2	1.6	2.48	1.41
CuBr	2.4	1.9	2.20	−0.54
CuCl	2.4 [a]	1.0	2.36	−2.34
100 K:				
CuI	2.1	1.7	2.55	4.26
CuBr	3.0	1.8	2.27	1.92
CuCl	•••	1.5	2.38	0.24
295 K:				
CuI	2.4	2.0	2.70	4.20
CuBr	•••	2.3	2.56	4.83
CuCl	•••	•••	2.58	5.55

[a] Reference 7.

TABLE II. Pressure dependence of frequencies of α, β, γ peaks of CuCl (cm^{-1}/kbar).

	α	β	γ
40 K		0.34	0.53
100 K		0.97	0.66
295 K	-0.04	0.15	0.28

for cubic crystals. The term on the left-hand side of Eq. (5) is the frequency change as a function of temperature at constant pressure. The first term on the right is the frequency change as a function of volume at constant temperature. Both of the above terms can be calculated from experimental data. The last term on the right-hand side, which therefore is determined, is the frequency change as a function of temperature at constant volume. The last term may not be obtained directly from experiment as volume changes accompany temperature changes.

The contributions to the temperature-dependent phonon frequencies on the right-hand side of Eq. (5) are both due to anharmonic interactions. Maradudin and Fein[19] and Cowley[15] have calculated these contributions for cubic and quartic anharmonicities. They showed that the anharmonicity leads to a phonon self-energy whose real part Δ is observed as a frequency shift of the phonon from its "harmonic" value, ω_i^H. They further showed that Δ can be separated into

$$\Delta = \Delta^E + \Delta^A , \qquad (6)$$

where Δ^E represents the anharmonic frequency shift due to thermal expansion and Δ^A represents the shift due to cubic and quartic anharmonicities. We are therefore able to relate the first term on the right-hand side of Eq. (5) with Δ^E and the second term with Δ^A.

Table III lists the terms of Eq. (5) for the phonon modes observed experimentally. The last two columns give the values of the volume and multiphonon contributions, respectively, to the isobaric temperature dependence of the mode frequency. It can be seen that in most cases in Table III the multiphonon term dominates the volume term. In these temperature regions, then, the major contribution to the temperature dependence of the phonon frequencies is the temperature dependence of the anharmonic coupling of the phonons. The exceptions are interesting: At 40 K, the TO and LO modes in CuI have equal volume and multiphonon contributions, and, at 100 K, the LO mode in CuBr has a larger volume term. We note that Potts et al. found the frequency of the LO mode in CuBr to decrease below 70 K as the temperature decreased. They suggested this decrease may mirror the negative thermal expansion of CuBr. Our data at 100 K shows that the volume dependence dominates multiphonon effects in the temperature dependence of the LO phonon frequency. However, at 40 K, multiphonon effects dominate the observed frequency shift. In fact, at temperatures where the thermal expansion changes from negative to positive, ~50 K in CuBr, β must be zero and the entire observed frequency change with temperature is due only to multiphonon effects and not to volume effects (as the volume is

TABLE III. Terms in Eq. 5.

	T (K)	ω_i (cm^{-1})	$\left(\dfrac{\partial \ln\omega_i}{\partial P}\right)_T$ (10^{-3}/kbar)	$\left(\dfrac{\partial \ln\omega_i}{\partial T}\right)_P$ (10^{-5}/K)		$=-\dfrac{\beta}{\kappa_T}\left(\dfrac{\partial \ln\omega_i}{\partial P}\right)_T$ (10^{-5}/K)		$+\left(\dfrac{\partial \ln\omega_i}{\partial T}\right)_V$ (10^{-5}/K)
CuI TO	40	132.9	5.4 ± 0.7	0	=	-3.1	+	3.1
	100	131.5	5.5 ± 0.3	-31.0	=	-9.2	–	21.8
	295	124.0	6.5 ± 0.6	-32.8	=	-10.1	–	22.7
CuI LO	40	150.8	3.9 ± 0.6	0	=	-2.2	+	2.2
	100	149.0	4.3 ± 0.4	-28.9	=	-7.2	–	21.7
	295	140.3	5.9 ± 0.7	-30.7	=	-8.2	–	22.5
CuBr TO	40	135.3	5.2 ± 0.5	-4.4	=	1.3	–	5.7
	100	134.2	6.7 ± 0.3	-20.1	=	-5.6	–	14.5
	295	120.8	5.5 ± 1.9	-95.9	=	-10.4	–	85.5
CuBr LO	40	169.9	4.2 ± 0.5	13.4	=	1.0	+	12.4
	100	170.4	4.1 ± 0.2	-2.9	=	-3.4	+	0.5
CuCl LO	40	209.5	2.3 ± 0.6	8.5	=	2.2	+	6.3
	100	210.1	3.5 ± 0.1	1.1	=	-0.4	+	1.5

independent of temperature). Thus at 40 and 50 K the decrease of the CuBr LO phonon frequency is due to multiphonon effects. By extension, it appears that the decrease at temperatures below 70 K is not connected to the negative thermal expansion.

Maradudin and Fein[19] and Cowley[15] also showed that Δ^A due to cubic anharmonic interactions is negative in the frequency region of the lattice modes considered here, while that due to quartic anharmonic interactions may be either positive or negative. Thus, when the temperature term in Table III is positive quartic anharmonic coupling dominates cubic anharmonic coupling. This occurs for the cases of TO and LO scattering in CuI at 40 K, LO scattering in CuBr at 40 and 100 K, and LO scattering in CuCl at 40 and 100 K. We note that because cubic and quartic terms may cancel, a small value of the multiphonon term does not necessarily imply small anharmonic coupling.

We turn now to the result that the TO and LO mode become less separated with pressure which implies that the effective charge is decreasing. Following Mitra and Namjoshi,[20] the logarithmic derivative of the Szigeti effective charge can be written as

$$\gamma_{Z*} = -\frac{1}{2} + \left(\gamma_{LO} \frac{\epsilon_0}{\epsilon_\infty} - \gamma_{TO} \right) \Big/ \left(\frac{\epsilon_0}{\epsilon_\infty} - 1 \right)$$
$$+ \frac{\gamma_{\epsilon_\infty}}{2} \left(\frac{2 - \epsilon_\infty}{2 + \epsilon_\infty} \right) ,$$

where

$$\gamma_{\epsilon_\infty} = \left(\frac{\partial \ln \epsilon_\infty}{\partial \ln V} \right)_T .$$

ϵ_∞ is obtained from values of piezooptic constants determined by Biegelson.[21] Because of the uncertainty in the values of ϵ_0 we have used the LST relation $\epsilon_0 / \epsilon_\infty = (\omega_{LO}/\omega_{TO})^2$ to eliminate ϵ_0. Values of γ_{Z*} are shown in Table IV.

We shall focus our attention on the 40 K data because this analysis is applicable to a harmonic lattice and is therefore most appropriate at low temperatures. These 40-K data show negative values of $\gamma_{Z*} \sim -1.3$ for CuI and CuCl. Similar values are found in alkali halides and other zinc-blende materials.[22,23] CuBr has a positive γ_{Z*} which is anomalous. This result may be related to the fact that the peak associated with the LO phonon in the Raman spectra of CuBr is asym-

TABLE IV. Negative volume logarithmic derivatives of the effective charge γ_{Z*}.

	40 K	100 K	295 K
CuI	−1.20	−0.33	−0.03
CuBr	0.36	−0.84	
CuCl	−1.51		

metric and changes shape with pressure and temperature (Fig. 3). Thus the measured frequency shifts of the peak may not be the frequency shifts of the "harmonic" LO phonon.

V. CONCLUSION

We have observed Raman scattering in CuI, CuBr, and CuCl at 40, 100 and 295 K under pressures from 1 to 7 kbar. Our pressure cell utilizes a new design for the sapphire windows. The sapphires are prestressed in a plug before being placed in the pressure cell. This allows a pressure seal to be obtained easily. Mode Grüneisen parameters have been obtained for the LO and TO phonons in cases where they are observed experimentally; they show interesting temperature effects which need theoretical clarification.

By combining temperature and pressure dependence of the phonon frequencies, we separated the temperature dependence into a volume effect and a multiphonon effect. As expected for these materials which have large anharmonicities, multiphonon effects dominate volume effects in the temperature dependence of the phonon frequencies for most cases. In particular, the decrease of the LO phonon frequency of CuBr with decreasing temperature at low temperature is not related to the negative thermal expansion of CuBr at these temperatures.

The logarthmic volume derivatives of the Szigeti effective charge have been determined. At 40 K, data for CuI and CuCl give reasonable numbers (by comparison to other materials) for these derivatives while data for CuBr gives a result with the wrong sign. We may not be obtaining the frequency of the "harmonic" LO phonon in CuBr because of the asymmetry of the observed peak.

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