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Temperature dependence of Raman scattering, electro-optic, and dielectric properties of CuBr

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The Raman spectra, the clamped electro-optic coefficient (r_{41}), the dielectric constant (κ), and refractive index (n) of CuBr have been measured as functions of temperature. The longitudinal (LO) and transverse (TO) Raman modes are easily identifiable at low temperatures and can be followed continuously to room temperature where two weak second-order modes are present. The TO mode has a strong temperature dependence which may be related to the high-temperature phase transition by a temperature-dependent ionicity. Both κ and r_{41} have a strong positive temperature dependence, whereas n is nearly independent of temperature. Fitting of a Sellmeier relation to refractive-index data allows a good value of n_∞ to be calculated. With n_∞, the temperature-dependent Raman frequencies allow a Lyddane-Sachs-Teller calculation of the temperature-dependent dielectric constant for comparison with the directly measured dielectric constants. The thermal behaviors of r_{41}, κ, and n are then used to derive nonlinear optical coefficients. The derived coefficients and directly measured ones agree reasonably well in magnitude, have the same algebraic signs, and show similar wavelength dependence.

I. INTRODUCTION

In a recent publication[1] we showed that the unusual temperature variation of the linear electro-optic coefficient r_{41} and the constant-strain dielectric constant κ in CuCl could be used to predict the magnitude and sign of the nonlinear optic coefficient d^{o}_{14}. We also measured the temperature behavior of the Raman spectrum and confirmed the existence of strong second-order bands which had previously been reported in Raman[2] and infrared[3] experiments and which make the interpretation of the spectrum difficult. The anomalous behavior of CuCl was illustrated by a comparison[1] with the behavior of GaAs which is representative of the large class of tetrahedrally coordinated binary semiconductors to which they both belong. Among the unusual features of CuCl are the strong temperature dependence of κ and r_{41}, the negative[1,4] sign of d^{o}_{14}, the comparable strengths of first- and second-order Raman and infrared bands, and the anomalous temperature behavior of these bands. In discussing the behavior of CuCl, we used the fact that the ionicity f_i of the bonding in this material is very high[5] and is, in fact, near the upper limit at which tetrahedral bonding is observed to occur.[6] In addition, the discussion made use of the way in which the loosely bound Cu d electrons alter[7] the charge distribution in the crystal. Since CuBr has nearly as large an ionicity ($f_i = 0.877$ vs 0.882 for CuCl) and should also show strong d-electron effects, we have investigated the temperature dependence of the Raman spectrum and the linear electro-optic effect in this material.

The Raman spectrum of CuBr, which is discussed in Sec. II, consists of only two dominant Stokes bands which are assigned to the transverse (TO) and longitudinal (LO) modes. This behavior is consistent with the simple behavior observed in earlier[3] infrared and recently published[8,9] Raman spectra, although our Raman spectra differ in some particulars from those previously published.[8]

Measurements of the constant-strain linear electro-optic coefficient at 0.633, 1.15, and 3.39 μm were made as a function of temperature and the sign of r_{41} was determined. The refractive index was measured from 0.55 to 10 μm at two temperatures, and the constant-strain dielectric constant was measured as a function of temperature. The results are included in Sec. III. Both κ and r_{41} change appreciably over the temperature range studied and, since both parameters are related to the same Raman- and infrared-active mode, their temperature variations can be used to separate the purely electronic and lattice-dependent components of r_{41}. Further calculation yields the sign and magnitude of d^{o}_{14}.

II. RAMAN MEASUREMENTS

The apparatus employed was the same as that used for the CuCl measurements.[1] Figure 1 shows spectra at five temperatures obtained with a He-Ne 0.633-μm laser source providing 12 mW in

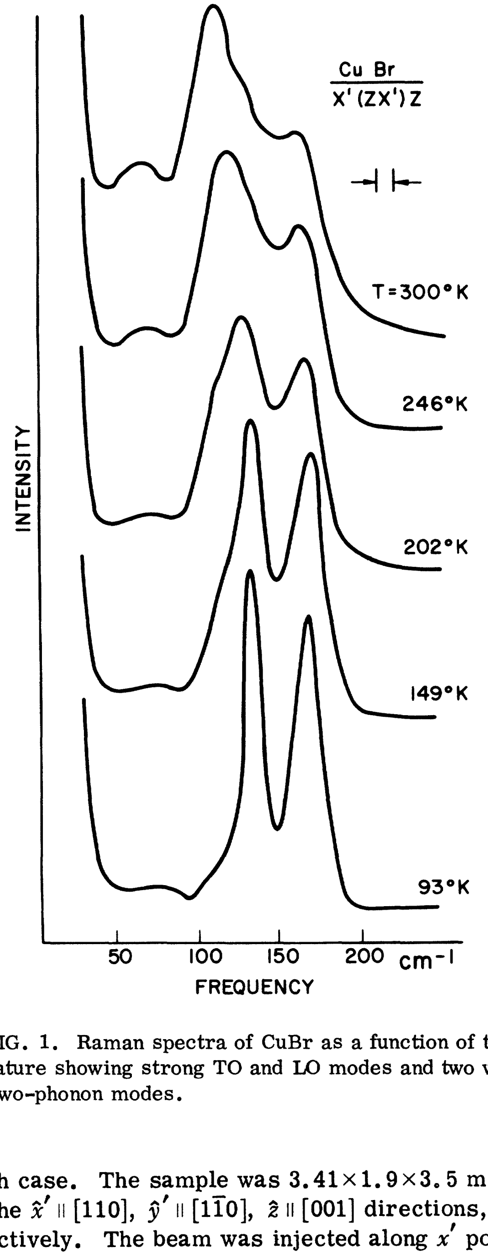

FIG. 1. Raman spectra of CuBr as a function of temperature showing strong TO and LO modes and two weaker two-phonon modes.

each case. The sample was 3.41×1.9×3.5 mm in the $\hat{x}'$ ‖ [110], $\hat{y}'$ ‖ [$1\bar{1}0$], $\hat{z}$ ‖ [001] directions, respectively. The beam was injected along x' polarized along z and the scattered beam was observed along z polarized along x'. Both longitudinal (LO) and transverse (TO) modes are allowed for this orientation. The spectrometer resolution was 10 cm^{-1}.

At 93 °K our observed spectra have only two prominent features which we identify as the LO and TO modes. The spectra agree well with the 4.2 °K results of Murahashi *et al.*[9] At higher temperatures, in addition to the strong LO and TO modes, two weak features become evident. These modes are similar to two-phonon sum and two-phonon difference modes observed by Prevot *et al.*[8] In our spectra, since the two-phonon modes are comparatively weak, the ambiguity in separating one- and two-phonon modes encountered with CuCl[1] does not arise. It can be seen in Fig. 1 that the weak two-phonon sum mode intersects the TO mode in the neighborhood of 246 °K. The modes are identified in Table I. Although the absolute strengths of the lines were not measured, a comparison with a 93 °K CuCl spectrum shows that the LO and TO modes have comparable strengths in the two materials.

As with CuCl, the transverse-mode frequency ω_T in CuBr decreases sharply as the temperature T increases. The temperature dependence of ω_T^2 is shown in Fig. 2. It can be seen that for a reasonable extrapolation

$$\omega_T^2 \sim (T_c - T) \qquad (2.1)$$

near $T_c \approx 664$ °K, the temperature at which CuBr undergoes a first-order transition from the zinc-blende γ phase to the wurtzite β phase. (Another transition to a body-centered-cubic α phase occurs at 743 °K.)[10] This temperature dependence is reminiscent of the "soft mode" observed in ferroelectrics near the Curie temperature T_C. In the ideal ferroelectric case, temperature-dependent long-range dipole forces weaken the effective spring constant, reducing ω_T^2 near T_C. As $T \rightarrow T_C$ the mode becomes unstable causing a second-order phase transition. In the present case, we postulate a temperature-dependent ionicity f_i that increases with T, possibly due to thermal expansion of the lattice which reduces the overlap of neighboring wave functions. As $f_i \rightarrow f_c$, the critical ionicity,[6] the ionic β (or α) phase becomes less energetic than the covalent γ phase and the transition occurs. The zinc-blende-to-wurtzite transition must be first order. However, for $f_i < f_c$, the characteristic frequency may anticipate the transition and behave as

$$\omega_T^2 \sim (f_c - f_i) \quad . \qquad (2.2)$$

[As in the ferroelectric case, the longitudinal mode frequency ω_L need not be singular at $f_c(T_c)$.]

III. ELECTRO-OPTIC AND DIELECTRIC MEASUREMENTS

A. Dielectric constant and refractive index

The dielectric behavior of CuBr is similar in several respects to that of CuCl.[1,11] The constant

TABLE I. Raman spectrum.

Temp. (°K)	Frequency (cm^{-1}) 2-phonon diff.	2-phonon sum	TO	LO
93	~74	~105	134	167
149	~73	~105	130	168
202	~72	~110	125	167
246	~67	⋯	119	166
300	~62	~124	111.5	161

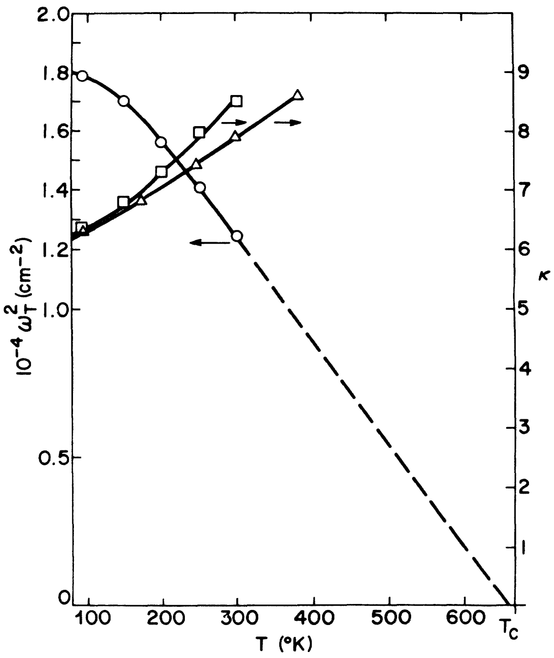

FIG. 2. Temperature dependence of ω_T^2 shown by circled data points—left-hand scale. The dashed curve is a linear extrapolation to the phase transition temperature T_c at ~664 °K. Dielectric constant κ on right-hand scale with square data points from LST relation and triangles from radio-frequency measurements.

strain dielectric constant obtained from either the Lyddane-Sachs-Teller (LST) relation or from direct measurement increases strongly with temperature. There are also similarities in the unusual low-frequency dielectric behavior; a large anomalous dispersion and a strong temperature dependence. The real part of the relative dielectric constant κ' at 1000 Hz varies from 9200 at room temperature to 92 at 90 °K while the imaginary part κ'' varies from 6000 to 15. At 400 Hz, κ' varies from 11 000 at room temperature to 75 at 90 °K and κ'' varies from 7000 to 35. These results were obtained after the crystal had been heated moderately and kept in vacuum for several days in order to reduce moisture. After a 4-day exposure to room air we measured $\kappa' = 13\,000$ and $\kappa'' = 40\,000$ at 1000 Hz, while at 400 Hz we measured $\kappa' = 25\,000$ and $\kappa'' = 90\,000$. This is the same curious behavior that Smakula[11] observed in CuCl and which he ascribed to moisture.

A radio-frequency bridge was used to measure high-frequency dielectric constants. At 295 °K, we found $\kappa = 7.9$ in the frequency range 10–55 MHz. The scatter in the measurements was unusually large (~ 7%), possibly due to recent sample history, and there may have been some frequency dependence at the low-frequency end of the range. Capacity measurements were made at five temperatures from 95 to 375 °K at frequencies of 10 and 15 MHz, since circuit limitations precluded use of higher frequencies when the sample was in a Dewar. The capacity increased smoothly with temperature and yielded values $\kappa = 6.4$ at 95 °K and $\kappa = 8.6$ at 375 °K as shown in Fig. 2. The absolute values of κ are probably accurate to 10% but the relative accuracy should be better.

Because of the uncertainties in the direct measurement of κ we have also calculated the dielectric constant from the LST-relation using our temperature-dependent Raman frequencies. In order to make use of the LST relation

$$\kappa = (\omega_L/\omega_T)^2\, n_\infty^2 \quad , \tag{3.1}$$

it is necessary to know the dispersionless refractive index n_∞, which would be appropriate to the spectral region well above ω_L and ω_T and well below the electronic resonance frequencies. The appropriate value of n_∞ was found by fitting a Sellmeier-type formula[12] to refractive-index data in the visible and near infrared and taking the long-wavelength limit but excluding lattice contributions. The relation

$$n^2 = 1 + \sum_{i=1}^{3} \frac{A_i}{1 - (B_i/\lambda)^2} \tag{3.2}$$

includes the effects of a polar lattice oscillator in the infrared. Using the values $A_1 = 0.1535$, $A_2 = 2.9082$, $A_3 = 0.06$, $B_1 = 0.399$ μm, $B_2 = 0.1777$ μm, and $B_3 = 16.6$ μm, Eq. (3.2) fits refractive-index values from published[13] data (0.4358–0.7699 μm) and our prism refractometer measurements (0.55–10 μm) to within five parts in the fourth decimal place. At wavelengths below 1 μm the fit is three parts in the fourth place. Since the infrared oscillator represents a lattice contribution,[14] we let $A_3 = 0$ and $\lambda \rightarrow \infty$ in Eq. (3.2) to find $n_\infty^2 = 4.06_2$. [A value of $n_\infty^2 = 3.7$ is given by Prevot *et al.*,[8] and $n_\infty^2 = 4.4$ by Plendl *et al.*[3]] With our value of n_∞ and Eq. (3.1), the relative dielectric constant is found to vary smoothly from 8.5 at 300 °K to 6.35 at 93 °K as indicated in Fig. 2.

Refractive-index measurements were also made at 122 °C. As in CuCl[1,15] the rate of change with temperature is small: $dn/dT = 7\times10^{-6}$ at 10 μm and increases smoothly to 10^{-5} at 0.8 μm. (There appears to be a narrow peak at about 0.75 μm in which dn/dT becomes greater than 2×10^{-5} before falling to 10^{-5} at 0.55 μm.)

The ratio ρ of ionic susceptibilities at 90 and 295 °K (two widely separated temperatures) will be used in later calculations:

$$\rho \equiv \frac{\kappa(90\,°\mathrm{K}) - n_\infty^2(90\,°\mathrm{K})}{\kappa(295\,°\mathrm{K}) - n_\infty^2(295\,°\mathrm{K})} \quad . \tag{3.3}$$

Using κ calculated from LST, we compute ρ

$= 0.516$. With κ from the direct measurements, $\rho = 0.611$.

B. Electro-optic sign determination

The sign of the electro-optic coefficient was found by determining both the sense of the electro-optic effect and the sense of the piezoelectric effect. Using anomalous x-ray scattering to determine the crystal configuration,[16] the sign of the piezoelectric coefficient of CuBr has been reported to be the same as that of CuCl which, in turn, has been found to be positive.[4] We use the now generally accepted convention that a positive [111] direction in the zinc-blende structure points from a metal (Cu) ion to a nearest-neighbor anion (Br).

The piezoelectric test was made by determining the polarity of the voltage developed between {001} faces when a stress is applied to a pair of {110} faces. Platinum-paste electrodes were used to contact the two opposite {001} faces. Either of these may be designated as the positive (001) face. By definition of a positive piezoelectric coefficient, a compressive force applied to the (110) and $(\bar{1}\bar{1}0)$ faces causes a negative voltage to be developed on the (001) face and conversely, a force applied to $(\bar{1}10)$ and $(1\bar{1}0)$ faces causes a positive voltage to be developed on the (001) face. Thus, having chosen the positive z direction, the piezoelectric test differentiates between x and y axes in a right-handed coordinate system. The positive sense of, say, the x axis can then be chosen arbitrarily fixing the sense of y and furnishing a coordinate system consistent with the earlier definition of a positive [111] direction.

In order to find the sign of the electro-optic coefficient, the same modulating voltage was applied to the CuBr crystal and a standard ($LiNbO_3$) crystal with the laser beam passing through both crystals in series. The resulting modulation index is simply the sum or difference, depending on the relative signs, of the modulation indices of the individual crystals and this index was measured using the heterodyne method. The sense of the c axis of the standard crystal is known and the r_{13} and r_{33} coefficients are known[17,18] to be positive. Experimental determination of whether the modulation produced in the CuBr crystal adds to or subtracts from that produced in the standard then fixes the sign of the electro-optic coefficient of CuBr.

C. Electro-optic measurements

Electro-optic measurements were made at 0.633, 1.15 and 3.39 μm using the heterodyne method. The modulating frequency was 50 MHz in nearly all the experiments although some measurements were made at frequencies up to 85 MHz to search for acoustic resonances. No frequency dependence was found, indicating a constant-strain measurement. The crystal used had (001), (110), and $(1\bar{1}0)$ faces. The modulating field was parallel to the [110] direction with propagation in the $[1\bar{1}0]$ direction and optical polarization in the $(1\bar{1}0)$ plane at either $+45°$ or $-45°$ to [001]. At 0.633 μm the crystal was noticeably birefringent. Some of this birefringence was evidently due to strains resulting from the necessary cutting and polishing operations and some was due to stresses applied by the crystal holder. The effects of the birefringence were minimized by using portions of the crystal which did not depolarize the beam appreciably—either because the birefringence was small or because a birefringent axis coincided with the polarization direction. Under these conditions the results obtained with polarizations at $+45°$ or $-45°$ to [001] were the same within experimental uncertainty.

The electro-optic coefficient was measured in the range 85–330 °K with the apparatus used in the CuCl experiments. As in those experiments, dielectric loss caused some problems, and modulating field strengths were limited to 500 V/cm at room temperature and 1000 V/cm at the lowest temperature because of heating.

At room temperature the measured constant strain electro-optic coefficient r_{41} was -3.0×10^{-12} m/V at 1.15 and 3.39 μm and -2.5×10^{-12} m/V at 0.633 μm with an uncertainty of ±20%. Figure 3 shows the temperature dependence of the 0.633-μm nonlinear coefficient d_{14}^{eo}, which is related[19] to r_{41} by

$$n^4 r_{41} = -4 d_{14}^{eo} \quad . \tag{3.4}$$

The experimental points in Fig. 3 were obtained on

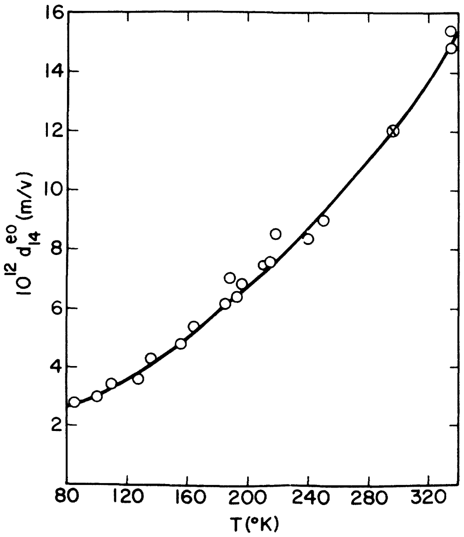

FIG. 3. Temperature dependence of d_{14}^{eo} electro-optic coefficient at 0.633 μm.

TABLE II. Summary of experimental results.

λ (μm)	r_{41} (10^{-12} m/V) 295 °K	r_{41} (10^{-12} m/V) 90 °K	d_{14}^{eo} (10^{-12} m/V) 295 °K	d_{14}^{eo} (10^{-12} m/V) 90 °K	R
3.39	−3.0	−1.2	+12.6	+5.0	0.39_5
1.15	−3.0	−1.2	+12.9	+5.0	0.39_4
0.633	−2.5	−0.6	+12.0	+2.8	0.24_3

three separate runs. Each point represents an average obtained using four or five different modulating voltages. Table II includes values of r_{41} and d_{14}^{eo} at 90 and 295 °K as well as the ratios R of their values at these temperatures, which will be needed later.

D. Derivation of nonlinear optical coefficients

The technique for calculating nonlinear optical coefficients described earlier[1] is outlined below.

The nonlinear coefficient d_{14}^{eo} is composed of two parts: the purely electronic optical mixing coefficient d_{14}^{o} and a lattice term d_{14}^{i} caused by the change in optical polarizability due to ionic motion. Thus, we write

$$n^4 r_{41} = -4 d_{14}^{eo} = -4\,(d_{14}^{o} + d_{14}^{i}) \quad . \tag{3.5}$$

Using the generalized[20,21] Miller coefficients

$$\delta_{14}^{C} = (\kappa - n_\infty^2)^{-1}\,(n^2 - 1)^{-2} d_{14}^{i} \tag{3.6}$$

and

$$\delta_{14}^{D} = (n_\infty^2 - 1)^{-1}\,(n^2 - 1)^{-2} d_{14}^{o} \quad , \tag{3.7}$$

we rewrite Eq. (3.5) as

$$n^4 r_{41}(T) = -4\,(n^2(T) - 1)^2 \times \{[\kappa(T) - n_\infty^2(T)]\,\delta_{14}^{C} + [n_\infty^2(T) - 1]\,\delta_{14}^{D}\} \quad , \tag{3.8}$$

where the temperature-dependent quantities are indicated explicitly. The quantities δ_{14}^{C} and δ_{14}^{D}, which are presumed to be temperature independent, can then be found from Eq. (3.8) if values of r_{41} and κ at two different temperatures are used. In terms of the experimental ratios R and ρ defined earlier,

$$\delta_{14}^{D} = \frac{d_{14}^{eo}}{(n^2 - 1)^2\,(n_\infty^2 - 1)}\;\frac{R - \rho}{1 - \rho} \quad , \tag{3.9}$$

$$\delta_{14}^{C} = \frac{d_{14}^{eo}}{(\kappa - n^2)\,(n^2 - 1)^2}\;\frac{1 - R}{1 - \rho} \quad , \tag{3.10}$$

where n, n_∞, κ, and d_{14}^{eo} are 295 °K values.

Table III presents the values of the ionic and electronic d and δ coefficients derived from the above relations. The results using dielectric constants derived from the LST relation and direct radio-frequency measurements are listed under LST and Dir, respectively. The difference in dielectric constants (~ 20%) leads to an ~ 100% change in the calculated electronic coefficient d_{14}^{o}. This is caused in part by the fact that d_{14}^{o} is a much smaller contributor to the electro-optic effect than the dominant lattice term. Recently measured[22] values of d_{14}^{o} found by optical second-harmonic generation (SHG) are included in Table III to allow comparison. Our calculated values have the correct sign and nearly all the calculated d_{14}^{o} lie within ~ 50% of the SHG d_{14}^{o}.

In addition to the assumed invariance with temperature, δ^D and δ^C are generally assumed to be independent of wavelength when not too near the band edge.[23] Our calculated δ^C values in Table III show no wavelength dependence. The infrared values of δ^D are also constant, but the 0.633-μm δ^D values are larger than the infrared values by ~ 40% (Dir) or 70% (LST). The SHG δ^D values whose measurement involve wavelengths above and below 0.633 μm are also ~ 50% higher than the longer-wavelength result. Since both SHG and calculated values of δ^D show this large dispersion in CuBr and since a somewhat similar situation exists with the CuCl[1] coefficients, there may indeed be anomalous wavelength dependence of δ^D.

TABLE III. Nonlinear coefficients of CuBr calculated from linear electro-optic and dielectric properties.

λ (μm)	d_{14}^{o} (10^{-12} m/V) LST	d_{14}^{o} Dir	d_{14}^{i} LST	d_{14}^{i} Dir	δ_{14}^{D} LST	δ_{14}^{D} Dir	δ_{14}^{C} LST	δ_{14}^{C} Dir
3.39	−3.2	−7.0	+15.8	+19.6	−0.11	−0.24	+0.37	+0.53
1.15	−3.3	−7.2	+16.2	+20.1	−0.11	−0.23	+0.36	+0.52
0.633	−6.8	−11.3	+18.8	+23.4	−0.19	−0.32	+0.36	+0.52
1.318 → 0.659	−4.86[a]		+16.6[b]		−0.13[a]			
1.064 → 0.532	−6.7[a]		+18.7[b]		−0.19[a]			
0.946 → 0.473	−6.8[a]		+18.8[b]		−0.17[a]			

[a] Reference 22.

[b] Using directly measured electro-optic coefficient at 0.633 μm and 295 °K with d_{14}^{o} values from Ref. 22.

IV. CONCLUSION

The relative index of CuBr is found to be relatively insensitive to temperature. However, the lattice related properties measured and calculated here have a strong dependence. It is postulated that this behavior is associated with an increase in ionicity with increasing temperature. Since the room-temperature ionicity is already close to the largest value for which the zinc-blende structure is allowed, a small increase has a large effect on lattice properties.

We have demonstrated that the thermal behavior of dielectric constant, refractive indices and electro-optic coefficient allow a satisfactory calculation of nonlinear optical coefficients. Even though the lattice contribution to the electro-optic coefficient is substantially larger than the nonlinear optical contribution, agreement between the directly measured nonlinear optic coefficients and those calculated from the measured electro-optic coefficient is quite good.

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[1] I. P. Kaminow and E. H. Turner, Phys. Rev. B 5, 1564 (1972).

[2] M. Krauzman, in *Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer-Verlag, New York, 1969).

[3] J. A. Plendl, A. Hadni, J. Claudel, Y. Henninger, G. Morlot, P. Strimer, and L. C. Mansur, Appl. Opt. 5, 397 (1966); A. Hadni, F. Brehat, J. Claudel and P. Strimer, J. Chem. Phys. 49, 471 (1968).

[4] R. C. Miller, S. C. Abrahams, R. L. Barns, J. L. Bernstein, W. A. Nordland, and E. H. Turner, Solid State Commun. 9, 1463 (1971).

[5] L. Pauling, *The Nature of the Chemical Bond* (Cornell U. P., Ithaca, N. Y., 1960); Phys. Today 24, 9 (1971).

[6] J. C. Phillips, Rev. Mod. Phys. 42, 317 (1970); J. A. Van Vechten, Phys. Rev. 182, 891 (1969); Phys. Rev. 187, 1007 (1969).

[7] B. F. Levine, Phys. Rev. B 7, 2591 (1973).

[8] B. Prevot, C. Carabatos, and M. Leroy, C. R. Acad. Sci. (Paris) 274, 707 (1972).

[9] T. Murahashi, T. Koda, Y. Oka, and T. Kushida, Solid State Commun. 13, 307 (1973); J. E. Potts, R. C. Hanson, C. T. Walker, and C. Schwab, Solid State Commun. 13, 389 (1973).

[10] J. Krug and L. Sieg, Z. Naturforsch. A 7, 369 (1952).

[11] A. Smakula (unpublished).

[12] A program due to J. D. Gabbe and G. D. Boyd was used to fit the formula.

[13] D. Chemla, P. Kupecek, C. Schwartz, C. Schwab, and A. Goltzene, IEEE J. Quantum Electron. QE-7, 126 (1971).

[14] Using data for CuCl from A. Feldman and D. Horowitz, J. Opt. Soc. Am. 59, 1406 (1969) as well as Ref. 13 and A. Feldman (private communication) similar three-oscillator Sellmeier parameters were found. Eliminating the lattice contribution, $n^2_\infty = 3.62$ for CuCl. The measured value at 22 μm is $n^2 = 3.33$.

[15] Yozo Kaifu and Teruo Komatsu, J. Phys. Soc. Jap. 25, 644 (1968).

[16] J.-C. Monier and R. Kern, C. R. Acad. Sci. (Paris) 241, 69 (1955).

[17] K. F. Hulme, P. H. Davies, and V. M. Cound, J. Phys. C 2, 855 (1969). This reference finds all the constant-stress coefficients to be positive.

[18] E. H. Turner (unpublished), quoted by G. D. Boyd and M. A. Pollack, Phys. Rev. B 7, 5345 (1973). In this work the constant-strain coefficients were found to be positive.

[19] G. D. Boyd and D. A. Kleinman, J. Appl. Phys. 39, 3597 (1968).

[20] C. G. B. Garrett, IEEE J. Quantum Electron. QE-4, 70 (1968).

[21] G. D. Boyd, T. J. Bridges, M. A. Pollack, and E. H. Turner, Phys. Rev. Lett. 26, 387 (1971).

[22] R. C. Miller, W. A. Nordland, S. C. Abrahams, J. L. Bernstein, and C. Schwab, J. Appl. Phys. 44, 3700 (1973).

[23] An apparent antiresonance in the deformation potential term has been observed as far as 1 eV from the band edge. This would affect the constancy of δ^C. The situation is described by J. L. Lewis, R. L. Wadsack, and R. K. Chang, in *Light Scattering in Solids* (Flammarion, Paris, 1971), p. 41. Also, J. F. Scott, T. C. Damen, and J. Shah, Optics Commun. 3, 384 (1971).