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Anharmonicity in CuCl—elastic, dielectric, and piezoelectric constants[*]

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Measurements have been made of the pressure and temperature dependence of the elastic, dielectric, and piezoelectric constants of cuprous chloride. Both shear elastic constants decrease with pressure with the $(c_{11} - c_{12})/2$ shear mode having the largest mode γ of -1.9. The piezoelectric constant increases 12% at a pressure of 10 kbar. The negative thermal expansion at low temperature is explained by the softening of all shear acoustic modes with pressure.

INTRODUCTION

In recent years the properties of crystals near the covalent-ionic "phase transition" have become of great interest. The cuprous halides and, in particular, CuCl are just on the covalent side of the critical ionicity of Phillips.[1] In an earlier paper[2] we showed that the cuprous halides have anomalously small elastic constants with the $(c_{11} - c_{12})$ shear constant approaching zero at the critical ionicity. In the present paper we present results on the pressure and temperature dependence of the dielectric and elastic constants of CuCl from which we also calculate information about the behavior of the piezoelectric constant. The large negative thermal expansion at low temperature is explained and comparison is made with other zinc-blende-structure compounds.

EXPERIMENTAL

The two crystals used in these investigations were the same as used in the earlier work.[2] They were grown by the travelling solvent method. Two basic measurements were made—elastic constants by pulse-echo ultrasonics and dielectric constant by ac-bridge or microwave-cavity methods. The behavior of the piezoelectric constant is inferred from the electromechanical coupling constant obtained from elastic constants measured with and without piezoelectric stiffening.

In a cubic crystal with T_d symmetry there is one piezoelectric constant, e_{14}. Shear waves propagating in $\langle 100\rangle$ are not piezoelectrically stiffened and are described by the elastic constant c_{44}^E while shear waves propagating in $\langle 110\rangle$ with polarization $\langle 001\rangle$ have an accompanying longitudinal electric field and hence the velocity is described by a stiffened elastic constant, c_{44}^D.[3] These two constants are related by

$$c_{44}^D = c_{44}^E[1 + (k'_{15})^2]$$

where k'_{15} is the electromechanical coupling constant for this case, which is given by

$$(k'_{15})^2 = e_{14}^2 / c_{44}^E \epsilon^s ,$$

where e_{14} is the strain piezoelectric constant and ϵ^s is the constant-strain, "clamped" dielectric constant. Thus, from measurements of these two elastic constants and the dielectric constant with changing pressure or temperature, the variation of the piezoelectric constant can also be determined.

The elastic-constant measurements were done by standard pulse-echo techniques using quartz transducers at 20 or 30 MHz. The pulse-superposition method[4] was used for determination of both absolute elastic constants and small changes. The modes measured were c_{11}, c_l for longitudinal waves propagating in $\langle 110\rangle$, $c_s = \frac{1}{2}(c_{11} - c_{12})$, c_{44}^D, and c_{44}^E. The pressure dependence of the elastic constants was measured with quartz transducers bonded to the crystal with Dow-Corning Silicone DC200. The hydrostatic pressure for both elastic and dielectric measurements was applied in a standard pressure vessel with argon gas as the pressure fluid. The pressure was measured with a manganin-resistance cell. The system was capable of 10 kbar, although in many cases leaks prevented the attainment of that pressure. The temperature of the sample was monitored with a Chromel-Alumel thermocouple inside the pressure vessel. After changing the pressure, measurements were made only after temperature equilibrium had been reached and small corrections were made for different equilibrium temperatures.

The temperature dependence of the elastic constants was measured using small $(2 \times 2$ mm$)$ 30-MHz quartz transducers bonded to the crystal with a "salol" solid bond, or with "Nonaq" grease. A temperature range of +30 to − 150 °C was covered with a few measurements to 50 and − 200 °C.

The temperature dependence of the dielectric

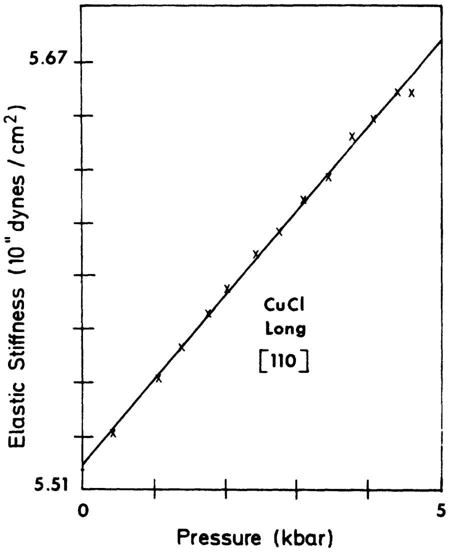

FIG. 1. Pressure dependence of c_l ⟨110⟩.

constant was measured by a microwave-cavity perturbation technique at 9.0 GHz. Detailed results and interpretation of this appear in another publication.[5]

The pressure dependence of the dielectric constant was measured by a standard three-terminal ac bridge. Considerable difficulty was experienced because of surface conductivity. This problem was solved by an evaporated guard ring connected to the ground terminal of the bridge. The sample used had a piezoelectrically driven length-expander mechanical resonance in the vicinity of 50 kHz. Difficulty was experienced in making measurements above this frequency presumably because of the large capacitance to ground in the pressure vessel. Measurements were made in the 10–20-kHz region without problems. The sample was mounted so it could freely vibrate and corrections were made to get values of ϵ^s.

RESULTS

Data are given for c_l, c_{44}^D, c_{44}^E, and c_s as a function of pressure in Figs. 1–4. The quantity $\rho_0 W^2$ is plotted versus pressure where ρ_0 is the density at ambient pressure and temperature and W is the wave velocity calculated using the unstressed length. These data were fitted by a least-squares method to first- and second-order polynomials. Only in the case of c_{44}^D was there a statistically significant need for the quadratic term. The results of these fits are shown in Table I with values for $c_0 = \rho_0 W^2$ $(p=0)$, and its first and second pressure derivatives being given. The first and second pressure derivatives of the adiabatic elastic constants are then calculated from this data using the method fo Cook[6] as modified by Chang and Barsch.[7] These results are also given in Table I. The uncertainty in the absolute value of elastic constants is 1%. The uncertainty in the first derivative value is 2% and the uncertainty in the second derivative is 15%.

The striking feature of these data is that all the shear constants decrease with pressure and also that c_{44}^D and c_{44}^E have a different behavior. The significance of this will be discussed later.

The results of the temperature dependence of the elastic constants indicate a normal linear softening with temperature in the range −150 to 30 °C for all of the modes except c_{44}^E, which exhibits unusual behavior by stiffening in the range − 200 to − 50 °C, then remaining relatively constant and

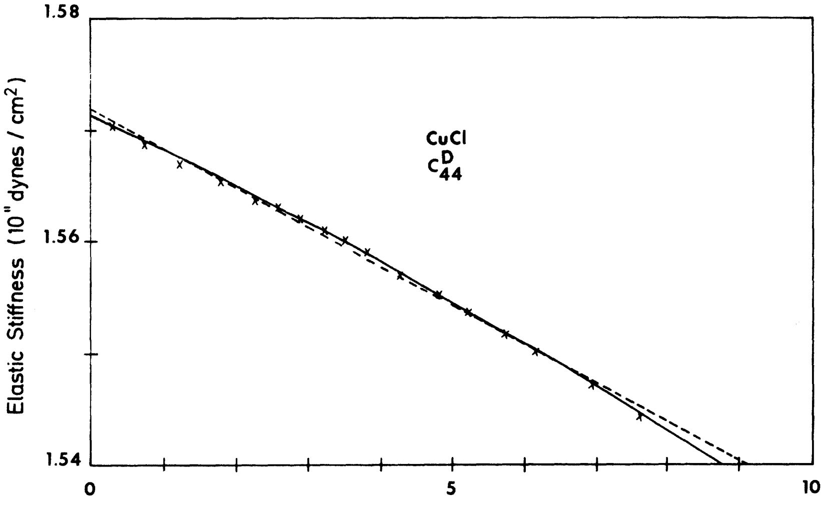

FIG. 2. Pressure dependence of c_{44}^D. Dashed line is best linear fit; solid line is best parabolic fit.

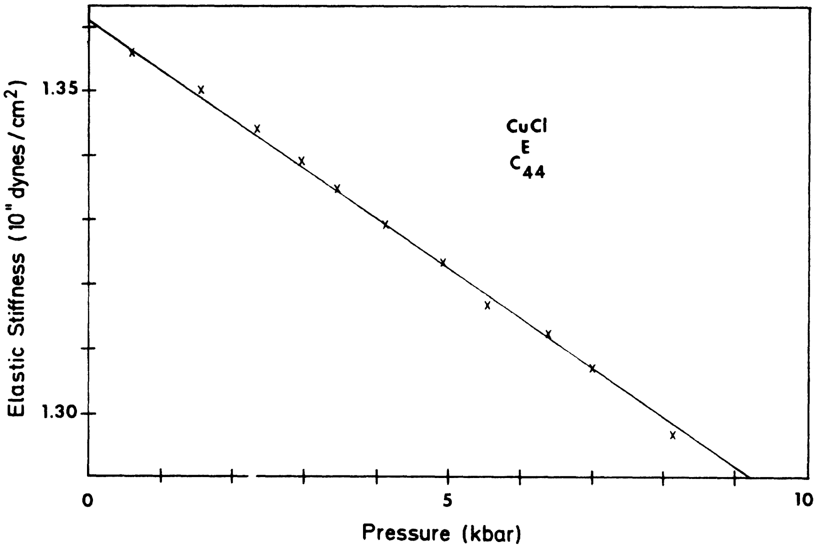

FIG. 3. Pressure dependence of c_{44}^E.

then softening again above 25 °C. This behavior is shown in Fig. 5. The logarithmic first temperature derivatives of $\rho_0 W^2$ and the elastic constants c are given in Table II, where a correction has been made for the thermal expansion.

The pressure dependence of the dielectric constant was determined on one run up to 3.5 kbar with the most reliable measurement being made at 10 kHz. With correction made for the difference between the constant-stress dielectric constant measured and the constant-strain dielectric constant needed, we obtain $d \ln \epsilon^s / dp = -3.5 \pm 0.2 \times 10^{-6}$ bar^{-1} with no evidence for any second derivative. Because of the difficulties mentioned previously, this must be regarded as the least-reliable measurement reported here. The temperature dependence of the dielectric constant as has been reported elsewhere is $d \ln \epsilon^s / dT = 8.0 \times 10^{-3}$ °K^{-1} in the range -200 to 20 °C.[5]

The pressure and temperature dependence of the electromechanical coupling constant can be determined from c_{44}^D and c_{44}^E. The pressure dependence at room temperature gives

$$(k_{15}')^2 = 0.127(1 + 3.26 \times 10^{-5} p - 3.1 \times 10^{-10} p^2),$$

where the pressure is given in bars. Using the assumed linear pressure dependence of the dielectric constant, we calculate the piezoelectric constant

$$e_{14} = 0.35(1 + 1.21 \times 10^{-5} p - 2.4 \times 10^{-10} p^2) C/M^2.$$

The uncertainty in e_{14} must be regarded as ±10% because of the dependence on the difference of c_{44}^D and c_{44}^E. Small variations in the choice of value for e_{14} will make a large difference in the values of the coefficients in the series expansion even though the coefficients are quite well determined for a particular choice of $c_{44}^D - c_{44}^E$.

The temperature behavior of the electromechanical coupling constant and the piezoelectric constant is complex. In the vicinity of the maximum in c_{44}^E we calculate $d \ln e_{14} / dT = -0.65 \times 10^{-3}$ °K^{-1}. From the estimated total change to 80 °K we calculate that e_{14} increases roughly 10% on going from 300 to 80 °K. A summary of these results is given in Table III.

DISCUSSION OF RESULTS

A. Thermal expansion

Cuprous chloride has a region of strong negative thermal expansion between 0 and 100 °K, as has

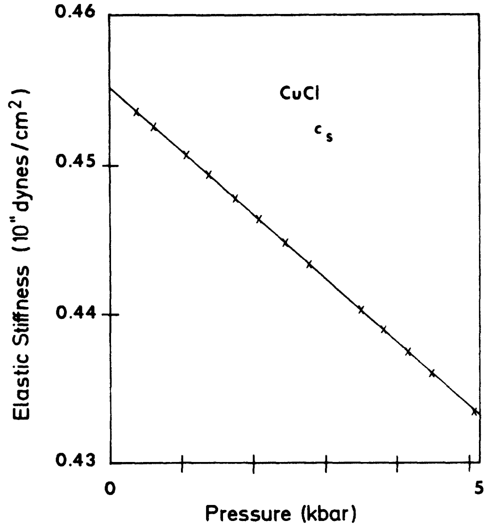

FIG. 4. Pressure dependence of $c_s = \frac{1}{2}(c_{11} - c_{12})$.

TABLE I. Pressure dependence of adiabatic elastic constants of CuCl.

Constant	$(\rho_0 W^2)_0$ $(10^6$ bar) $\pm 1\%$	$(\rho_0 W^2)'_0$ $\pm 2\%$	$\frac{1}{2}(\rho_0 W^2)''$ $(10^{-6}$ bar$^{-1})$ $\pm 15\%$	$\frac{dc}{dp}$ $\pm 2\%$	$\frac{1}{2}\frac{d^2c}{dp^2}$ $(10^{-6}$ bar$^{-1})$ $\pm 15\%$
c_{11}	0.454	3.31	0	3.69	−0.6
$c_l\langle 110\rangle$	0.552	3.13	0	3.59	−1.5
$c_s = \frac{1}{2}(c_{11} - c_{12})$	0.0455	−0.426	0	−0.388	−0.7
$c_{44}^D\langle 110\rangle$	0.1535	−0.305	−6.2	−0.176	−7.5
$c_{44}^E\langle 100\rangle$	0.136	−0.772	0	−0.658	−1.7

been shown by Schaake.[8] The lattice parameter goes from 5.40930 Å at 4.2 °K to 5.40676 Å at 77 °K to 5.41613 Å at 299 °K. The linear thermal expansion determined from his data at 300 °K is $\alpha = 1.54 \times 10^{-5}$ °K^{-1}. We calculate from his data a Grüneisen γ of 0.86 at 300 °K, using the Dulong and Petit value of heat capacity. His data are not adequate enough to permit a determination of the value of the Grüneisen γ in the interesting negative-thermal-expansion region.

We use the method of Daniels[9] to calculate the pressure dependence of Θ_D from our data on pressure dependence of the elastic constants. From this, we estimate the limiting low-temperature value of the thermal Grüneisen γ to be −1.42. In doing this, we have used c_{44}^E. This is not in disagreement with the low-temperature thermal-expansion data, but better thermal-expansion data are needed to effect a meaningful comparison.

We have not obtained a high-temperature value of the elastic Grüneisen γ because clearly one needs to know the pressure dependence of all the modes and, in particular, the optic modes to make a realistic estimation of the high-temperature thermal expansion.

One should note that, in principle, a more complicated calculation than has generally been done is needed both in this case and in the heat-capacity Θ_D calculation, because of the presence of a sizeable piezoelectric effect which stiffens many of the phonons in a way that is not included in the usual methods of calculation of Θ_D from elastic constants. Cuprous chloride would be an ideal material in which to test a better theory, because of the large electromechanical coupling constant. An idea of the size of the effect expected can be estimated by using the de Launay tables,[10] which with c_{44}^E gives $\Theta_D = 141$ °K while c_{44}^D gives $\Theta_D = 151$ °K where the 300 °K elastic constants have been used. No low-temperature specific-heat measurements of CuCl have been reported. These along with low-temperature values of the elastic constants would be necessary to make a comparison.

B. Phase transitions and force constants

Cuprous chloride has phase transitions at room temperature at 55 and 100 kbar. The c_s elastic constant extrapolates to zero at approximately 120 kbar. This steep decrease is probably a precursor of one of these phase transitions.

To compare materials we have calculated the *mode* Grüneisen γ's for the bulk modulus B, and the two shear constants c_{44} and c_s for a number of zinc-blende-structure materials whose pressure

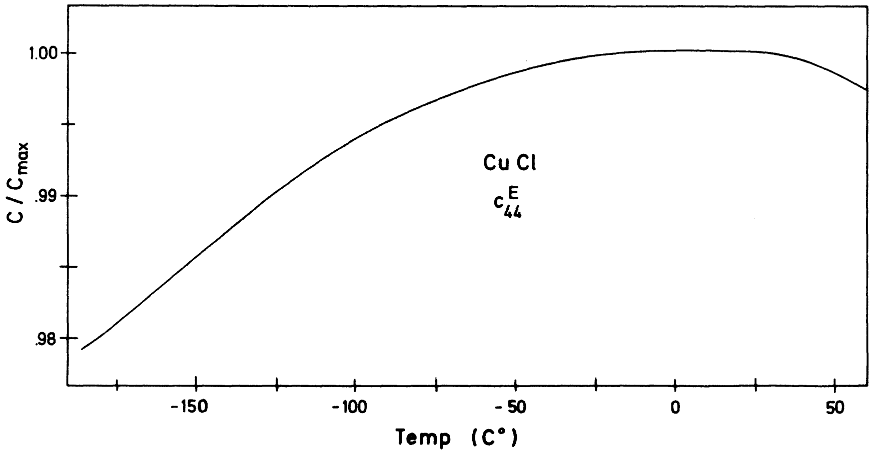

FIG. 5. Temperature dependence of c_{44}^E; line indicates experimental data.

TABLE II. Temperature dependence of adiabatic elastic constants of CuCl; $T = 25°\mathrm{C}$.

Constant	$\frac{d\ln(\rho_0 W^2)}{dT}$ ($10^{-4}\,°\mathrm{K}^{-1}$) ±2%	$\frac{d\ln c}{dT}$ ($10^{-4}\,°\mathrm{K}^{-1}$) ±2%
c_{11}	−7.30	−7.45
c_s	−1.50	−1.65
c_{44}^E	(see Fig. 5)	
c_{44}^D	−3.20	−3.35

derivatives of elastic constants have been reported. These data are given in Table IV. The bulk modulus has a γ of nearly 2 in all these materials. However, we note that the shear constants and particularly c_s have increasingly more negative γ's for materials of higher ionicity. Cuprous chloride is the first material which has a negative γ for both shear constants and has the largest negative γ for c_s.

We have used the simple lattice-dynamical model of Martin[11] to gain an insight as to the behavior of microscopic force constants under hydrostatic pressure. Using a pressure of 10 kbar as a standard (where the lattice parameter has decreased by nearly 1%) we find that α, the stretching force constant, increases by 8% while β, the bending force constant, decreases by 11%. At the same time, the internal-strain parameter increases only 2%. This model, having only two adjustable parameters, gives for c_{44} a ratio of experimental to theoretical values of 1.26 at 1 bar. However, this ratio has only changed to 1.25 at 10 kbar, indicating that the basic idea is correct and we are seeing a drastic decrease in the bending force constant in cuprous chloride as the ions are forced close to each other. This suggests that the bonding is becoming more ionic, as the ions are forced together with much less fractional electronic charge in the directed covalent bonds.

TABLE III. Collected data on cuprous chloride at 300 °K.

Thermal expansion[a]	$1.54\times10^{-5}\,°\mathrm{K}^{-1}$
B^S	3.93×10^{11} (dyn/cm^2)
B^T	3.98×10^{11} (dyn/cm^2)
c_{11}	4.54×10^{11} (dyn/cm^2)
c_{12}	3.63×10^{11} (dyn/cm^2)
c_{44}^E	1.36×10^{11} (dyn/cm^2)
c_{44}^D	1.535×10^{11} (dyn/cm^2)
ϵ^s/ϵ_0[b]	7.9
$\frac{d\ln\epsilon^s}{dT}$	$1.02\times10^{-3}\,°\mathrm{K}^{-1}$
$\frac{d\ln\epsilon^s}{dp}$	$-3.5\times10^{-6}\,\mathrm{bar}^{-1}$
e_{14}	$0.35\,(C/M^2)$
$\frac{d\ln e_{14}}{dT}$	$-0.90\times10^{-3}\,°\mathrm{K}^{-1}$
$\frac{d\ln e_{14}}{dp}$	$1.21\times10^{-5}\,\mathrm{bar}^{-1}$
$\frac{d\ln e_{14}}{d\ln V}$	−4.8

[a] Reference 8. [b] Reference 12.

TABLE IV. Mode Grüneisen parameters from elastic constant data for zinc-blende structure crystals.

Compound	f_i[a]	Mode γ B	c_s	c_{44}
GaAs[b]	0.310	2.25	−0.05	0.47
InSb[c]	0.321	2.28	−0.4	0.18
InAs[c]	0.357	2.22	−0.5	0.13
ZnTe[d]	0.546	2.35	−0.42	0.20
ZnS[e]	0.623	2.1	−0.87	0.21
ZnSe[d]	0.676	2.21	−0.38	0.16
CuCl[f]	0.746	2.0	−1.87	−1.13 (const. E) −0.39 (const. D)

[a] Ionicity according to Phillips, Ref. 1.

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The large discrepancy in the Lyddane-Sachs-Teller ratio and the large temperature dependence of the static dielectric constant has been explained as being due to the presence and large temperature dependence of a strong second-order phonon absorption in addition to the normal transverse-optical one-phonon absorption.[5,12] Presumably, one must also have large anharmonic contributions to the microscopic force constants to explain the strong temperature and pressure dependence of the constants reported here.

C. Piezoelectric effect

The behavior of the coupling constant k'_{15} and the piezoelectric constant e_{14} under hydrostatic pressure is quite striking. The constant e_{14} increases by 12% at 10 kbar. Also present is the second-derivative term which is in the opposite direction to the linear term. Presumably, at higher pressures other nonlinearities may become evident. Converted to a derivative with respect to fractional volume change the linear term becomes $d\ln e_{14}/d\ln V = -4.8$.

Jones[13] has measured the hydrostatic pressure dependence in quartz and obtains $d\ln d_{11}/d\ln V = -2.4$. Graham[14,15] has measured the *linear* strain dependence in quartz and lithium niobate and obtains $d\ln e_{11}/d\eta = -15.4$ (quartz) and $d\ln e_{33}/d\eta = -10$ ($\mathrm{LiNbO_3}$). Note that in all these cases the piezoelectric constant increases with decreasing volume.

Present theories of the piezoelectric effect involve a rigid-ion term and an offsetting charge transfer term. In Martin's[16] formulation $(a^2/e)e_{14} = \zeta Z_T^* - \Delta Q$, where a is the cubic cell constant, e is the electronic charge, ζ is the internal strain, Z_T^* is the transverse effective charge and ΔQ is the quadrupolar term which represents the charge transfer from positive to negative ion upon straining. As we showed earlier,[2] in cuprous chloride this ΔQ term is only about 18% of the pure ionic term. This is the smallest that this term is in any material indicating that CuCl is nearly a pure case of rigid-ion piezoelectricity. Under a hydrostatic pressure of 10 kbar the internal strain increases by 2% as calculated from Martin's theory,[11] while the effective charge is estimated[17] to decrease approximately 1% using preliminary values of the mode γ's for the optic modes.[18] These do not explain the 12% increase in e_{14} so one must assume that the charge transfer term is becoming drastically smaller. Again, as in the case of the elastic constants, this is an indication that the bonding is becoming more ionic with much-less-fractional electronic charge in the covalent bonds.

CONCLUSIONS

The pressure and temperature dependence of the elastic, dielectric, and piezoelectric constants in cuprous chloride have been measured. Both shear elastic constants decrease with applied hydrostatic pressure which reflects a strong weakening of the bending force constant in this crystal. The large negative thermal expansion in this material at low temperatures is explained by this. The piezoelectric constant is observed to increase under hydrostatic pressure. The decrease in bending force constant and the increase in the piezoelectric constant may be an indication that the crystal is becoming more ionic with decreasing lattice parameter.

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