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Dilatometric determination of piezoelectric constants: application to Cu(I)-halides

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A dynamic dilatometer for measuring piezoelectric strain constants of insulators and semiconductors is described. The application of modulation techniques allows precise measurements on samples as small as 1 mm^3 and of fairly high electrical conductivity. Results for the piezoelectric constants of zinc-blende type CuCl, CuBr and CuI are reported. The piezoelectric behaviour is related to properties of the chemical bond.

1. Introduction

Among the standard methods to measure piezoelectric constants of insulators are the determination of resonance and antiresonance frequencies of piezoelectric vibrators and the measurement of charge or voltage induced by strain [1]. In semiconducting materials, when the piezoelectric polarization is effectively screened by free carriers, the piezoelectric Hall effect can be used to obtain the piezoelectric coefficients [2]. The converse piezoelectric effect, which consists in straining the crystal by application of an electric field, has not been as frequently employed to determine piezoelectric constants [1].

In this paper we describe a simple dilatometer which uses a capacitor transducer and lock-in techniques to measure small sample strain caused by electric fields. The method can be applied to very tiny samples (as small as 1 mm^3), whose electrical conductivity may range within wide limits. Therefore, it is particularly useful for investigation of materials not available as large single crystals of high quality. As an application, we report measurements of the piezoelectric constants for the cuprous halides CuCl, CuBr and CuI.

The Cu(I)-halides are interesting because they are members of a large family of binary compounds which crystallize in the zinc-blende or wurtzite structures. An important parameter to characterize these compounds is their ionicity. In the spectroscopic ionicity scale introduced by Phillips [3] the Cu(I)-halides are located near the maximum value of ionicity compatible with tetrahedrally co-ordinated structures. Compounds with still larger ionicity tend to crystallize in the rock salt or caesium chloride structures. To test predictions of physical properties based on the ionicity scale [3] it is desirable to complete the knowledge of material constants of these highly ionic compounds.

2. Experimental

2.1. Dilatometer description

The mechanical construction of the dilatometer is sketched in Fig. 1. The lower end of the strained sample is held fixed by a support, the displacement of the upper end is transferred to a

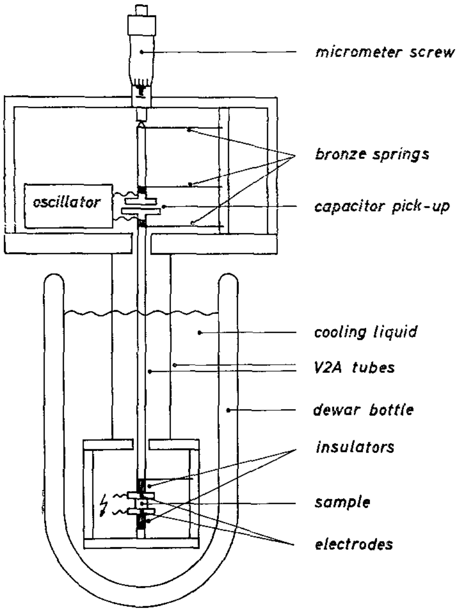

Figure 1 Mechanical dilatometer construction.

capacitor pick-up which is part of a VHF oscillator circuit. A change in sample length results in an oscillator frequency change which can be measured with high accuracy. For calibration, the gap between the condensor plates is varied in definite steps with a micrometer screw. Depending on the mounting of the sample electrodes, longitudinal or transverse strain with respect to field direction can be measured. With suitable sample cuts, it is possible to determine all of the 18 piezoelectric coefficients in the most general case of a triclinic crystal. The sample temperature can be changed by immersing the lower dilatometer part into various cooling liquids.

The electronic set-up for a dynamic operation of the dilatometer is described in Fig. 2. A low frequency (20 Hz) sinusoidal voltage from an audio oscillator is applied to the sample. The periodic strain modulates the VHF oscillator frequency. The mean frequency, f, is measured with a frequency counter. The frequency deviation, Δf, is found by demodulation of the signal in an FM radio tuner combined with a phase sensitive detector, which is locked to the audio oscillator. An automatic frequency control (AFC) stabilizes the tuner to the linear part of the system's demodulation characteristic.

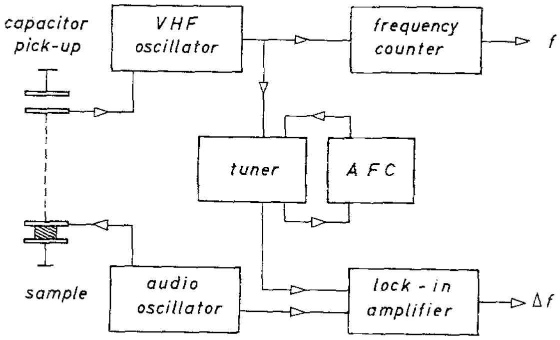

Figure 2 Electronic block diagram.

Absolute calibration of the whole set-up is performed by recording the oscillator frequency, f, as a function of the micrometer screw displacement, x. The sample length change, Δx, which corresponds to a given tuner signal output is then obtained from the demodulator characteristic of the tuner and by interpolating the function $f(x)$. The overall accuracy of this static calibration is estimated to be better than 1% if the operating frequency is sufficiently below any resonances of the mechanical transducer construction. The final sensitivity limit of the dilatometer depends on environmental noise, a lower limit being about $\Delta x = 10^{-10}$ cm.

An important advantage of the modulation technique compared to static measurements is its capability to separate piezoelectric strain from strain caused by electric heating of the sample. Since the phase sensitive detector is tuned to the frequency of the electric field, but the sample temperature is modulated with twice this frequency, the system will only respond to the polar piezoelectric effect. For this reason, piezoelectric measurements can also be performed on low ohmic materials, as far as a homogeneous field can be maintained in the specimen. Therefore, good ohmic contacts have to be prepared at the sample surface.

2.2. Sample preparation

The cuprous halide single crystals were orientated with the help of cleavage and prepared by cutting and grinding. Some attention is necessary to avoid twinned samples. Electric contacts were prepared with silver paint. Fringing of the electric field was reduced by imbedding the sample between projecting electrodes. A convenient sample geometry is found by an analysis of the piezoelectric tensor.

In the zinc-blende structure, the piezoelectric matrix d_{ik} has only one independent component $d_{14} = d_{25} = d_{36}$, other components vanish. For an electric field of strength E directed along the unit vector (α, β, γ) the sample strain tensor reduces to the form [4]

$$\hat{S} = \tfrac{1}{2}\begin{pmatrix} 0 & \gamma & \beta \\ \gamma & 0 & \alpha \\ \beta & \alpha & 0 \end{pmatrix} d_{14} \cdot E\,. \qquad (1)$$

Hence, the piezoelectric constant d_{14} is given by

$$d_{14} = \frac{\Delta x/x}{E(\alpha'\beta'\gamma + \beta'\gamma'\alpha + \gamma'\alpha'\beta)} \qquad (2)$$

where $\Delta x/x$ is the relative sample dilation along the direction $(\alpha', \beta', \gamma')$.

It is most convenient to choose field directions where a longitudinal piezoelectric effect appears, for example $\alpha = \beta = \gamma = \alpha' = \beta' = \gamma' = 1/\sqrt{3}$. In that case Equation 2 simplifies to

$$d_{14} = \sqrt{3}\Delta x/V \qquad (3)$$

where V is the voltage applied to the sample. As an additional advantage, a small misorientation of the sample will only cause a negligible error of d_{14} in this configuration. For example, a deviation of as large as 5° will only result in an error of 2%.

3. Results

Table I contains the piezoelectric strain constant d_{14} for three Cu(I)-halides as determined by the dilatometric method. The results are averages from at least five different samples for each compound. The error limits are determined essentially by the quality of the sample material available. Identical values of d_{14} were found at room temperature and at liquid nitrogen temperature, within the experimental accuracy. The absolute sign of the piezoelectric constants was not determined. For CuCl it is known that the sign is positive [5].

Table I also lists the piezoelectric constants $e_{14} = d_{14} \cdot c_{44}{}^{E}$, $g_{14} = d_{14}/\epsilon^{T}$ and $h_{14} = d_{14} \cdot c_{44}{}^{E}/\epsilon^{S}$ calculated from the measured d_{14}, the elastic stiffness $c_{44}{}^{E}$ and the permittivities ϵ^{T} and ϵ^{S} [4]. The elastic constants were taken from Hanson *et al.* [6], the dielectric constants from Plendl *et al.* [7]. Error limits of g_{14} and h_{14} are not quoted, because of uncertainties in the ϵ values.

The piezoelectric constants of the cuprous halides were recently determined with the resonator method by Inoguchi *et al.* [8] (CuCl) and by Hanson *et al.* [6] (CuCl, CuBr, CuI). The CuCl values obtained by these two groups differ by about 30%. The measurements presented in this paper are in favour of the low temperature values by Hanson *et al.* [6], with which they are in excellent agreement. However, it should be realized that we could not reproduce the marked decrease (~ 17%) of the CuCl value at room temperature which was observed by Hanson and co-workers. It seems that even a small sample conductivity will induce errors in the determination of piezoelectric constants with the resonator method. As outlined above, sample conductivity will cause less problems with the method described here.

4. Discussion

A variety of models for the microscopic origin of piezoelectricity has been discussed in the past [9]. As outlined by Arlt and Quadflieg [2] the piezoelectric effect may be decomposed into three different microsopic contributions, namely the generation of a polarization by the displacement of the ions, by electronic polarization, and by change of ionicity. These three contributions are of the same order of magnitude and tend to cancel each other [2]. For this reason it is difficult to predict the sign and magnitude of piezoelectric constants quantitatively on the basis of a first principles calculation, since the different contributions cannot be determined with sufficient accuracy.

An alternative way is the use of phenomenological models of piezoelectricity. In this case, model parameters are fitted to experimental data. One is then primarily interested in systematic trends of these parameters with properties of the chemical bond, e.g. with the ionicity of the compound. Relations of this kind were first suggested by Birman [10] and were discussed for tetrahedrally bonded III-V and II-VI compounds by Phillips and Van Vechten [11]. Inclusion of the cuprous halide results will allow to extend these considerations to I-VII-compounds.

For a discussion of systematic trends in piezoelectric constants we use a phenomenological model of piezoelectricity suggested by Birman [10]. In this approach, the chemical bond between two nearest neighbours is characterized by a bond dipole moment $\mu(r)$ which is always directed along the bond and changes its magnitude with the bond length r. In the tetrahedrally co-ordinated zinc-blende structure the different bond moments cancel in the unstrained state. In a strained crystal this is no longer the case, and a net polarization arises because of bond bending and bond stretching.

Birman derived the following expression for the piezoelectric stress constant e_{14} of the zinc-blende lattice:

$$e_{14} = \left\{ 4\gamma_{14} q_{\mathrm{s}} - (q_{\mathrm{s}} - q_{\mathrm{d}}) \frac{r_0}{\sqrt{3}} \left(\frac{4\gamma_{14}}{\sqrt{3} r_0} + \frac{4}{3} \right) \right\} \sigma_{\mathrm{t}} \,. \tag{4}$$

TABLE I Piezoelectric constants of the cuprous halides (mks units)

Material	d_{14} (m V^{-1})	e_{14} (C m^{-2})	g_{14} (m^2 C^{-1})	h_{14} (V m^{-1})
CuCl	$(2.72 \pm 0.05) \times 10^{-11}$	$(3.70 \pm 0.10) \times 10^{-1}$	4.10×10^{-1}	5.57×10^{9}
CuBr	$(1.60 \pm 0.10) \times 10^{-11}$	$(2.22 \pm 0.15) \times 10^{-1}$	2.26×10^{-1}	3.14×10^{9}
CuI	$(0.70 \pm 0.10) \times 10^{-11}$	$(1.27 \pm 0.20) \times 10^{-1}$	0.52×10^{-1}	0.95×10^{9}

Here, r_0 is the initial bond length, γ_{14} is the nonvanishing component of the relative internal strain tensor, σ_t is the density of elementary tetrahedra, and q_s and q_d are two parameters to characterize the bond. The "static effective charge" q_s is defined by $q_s = \mu(r_0)/r_0$ and the "dynamic effective charge" q_d by $q_d = (\partial\mu/\partial r)(r_0)$.

It would be possible to determine the bond parameters q_s and q_d from known values of e_{14}, r_0 and γ_{14} if an additional relation involving q_s and q_d were available. We obtain such a relation by expressing the transverse optic charge e_T (Born's charge) in terms of the effective charges q_s and q_d. The transverse charge e_T is defined by $\boldsymbol{\mu}_T = e_T\,\mathbf{u}$ where $\boldsymbol{\mu}_T$ is the dipole moment per tetrahedron induced by a displacement, $\mathbf{u}$, between the two sublattices of the zinc-blende structure, moved in the absence of an internal macroscopic field. It is related to experimentally observable quantities by

$$e_T{}^2 = \frac{M\omega_T{}^2}{4\pi\sigma_t}\cdot(\epsilon_0 - \epsilon_\infty) \tag{5}$$

where M is the reduced mass of an ion pair, ϵ_0 and ϵ_∞ are the static and high frequency dielectric constants, and ω_T is the angular frequency of the transverse optic mode. In the Birman model we find for the transverse charge

$$e_T = -\frac{8}{3}q_s - \frac{4}{3}q_d\,. \tag{6}$$

Note that both the piezoelectric constant e_{14} and the effective charge e_T were calculated with the same boundary condition, namely that the macroscopic electric field vanishes. No local field corrections were applied; we assume them to be incorporated into q_s and q_d.

With respect to more recent work [11, 12] Birman's result and Equation 6 will be rewritten in a slightly different form. We eliminate $r_0 = a\sqrt{3}/4$, $\sigma_t = 4/a^3$ and $\gamma_{14} = -\zeta a/4$ with the help of the cubic lattice constant a and Kleinman's bond bending constant ζ. Because there are four bonds per atom we introduce the static charge per metal ion $Q_s = -4q_s$ instead of the static charge q_s per bond. The metal ion is put into the origin of the zinc blende co-ordinate system. It is further convenient to define an effective charge redistribution exponent δ through the relation $\mu(r) = q_s(r/r_0)^{\delta}\cdot r$ in analogy to Phillips and Van Vechten [11]. The dynamic charge is then given by $q_d = (\delta + 1)\,q_s$ and we finally get

$$e_{14}a^2 = Q_s\left\{\frac{\delta}{3}(\zeta - 1) + \zeta\right\} \tag{7}$$

and

$$e_T = Q_s\left(\frac{\delta}{3} + 1\right) \tag{8}$$

substituting Equations 4 and 6. The influence of the various bond changes on the piezoelectric behaviour may now be seen more clearly. For $\zeta = 1$ the crystal shows pure bond bending [12], with no changes in bond lengths. In this case the charge redistribution term vanishes and only the static charge contributes to $e_{14}a^2$. For $\zeta = 0$ the internal strain vanishes and the bond geometry is altered by external strain alone. Under this condition a movement of the bond charges without charge redistribution does not give rise to a net polarization. It is the redistributed charge within the bonds which leads to a piezoelectric polarization in this case. In general, ζ is near $\zeta = 0.7$ [13] so that both the static and redistributed charge contribute to e_{14}.

Equation 7 for the piezoelectric constant e_{14} is different from the result obtained by Phillips and Van Vechten [11]. As already pointed out by Martin [15] the electric boundary condition connected with the definition of e_{14} does not allow to associate Callen's effective charge [14] with the internal strain term of e_{14}. According to Martin [15], and as seen above by inspection of Equations 7 and 8, it is the transverse optic charge e_T which is connected with the internal strain term ζ.

Fig. 3 shows a histogram plot of the static charge Q_s and the charge redistribution exponent δ versus the spectroscopic ionicity f_I [3, 16] for various III-V and II-VI compounds and the I-VII cuprous halides. Q_s and δ were calculated with the help of Equations 7 and 8 using e_{14}, ζ and e_T data for the III-V and II-VI compounds as listed* by Martin [15]. The cuprous halide values for e_T and ζ were determined from infra-red data by Plendl *et al.* [7] and from elastic constants by Hanson *et al.* [6]. Equation 5 was used to determine e_T and Martin's phenomenological model [13] served to calculate ζ.

It is seen in Fig. 3 that the model parameters Q_s and δ show definite trends with ionicity. For purely ionic binding ($f_I = 1$), the static charge Q_s reaches the limiting value $Q_s = 1\,e$, whereas the charge redistribution exponent δ becomes zero. For purely covalent binding ($f_I = 0$), one

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*ZnO data ($Q_s/e = 1.25$, $\delta = 2.04$, $f_I = 0.616$) are omitted in Fig. 3 for the reason quoted in [11].

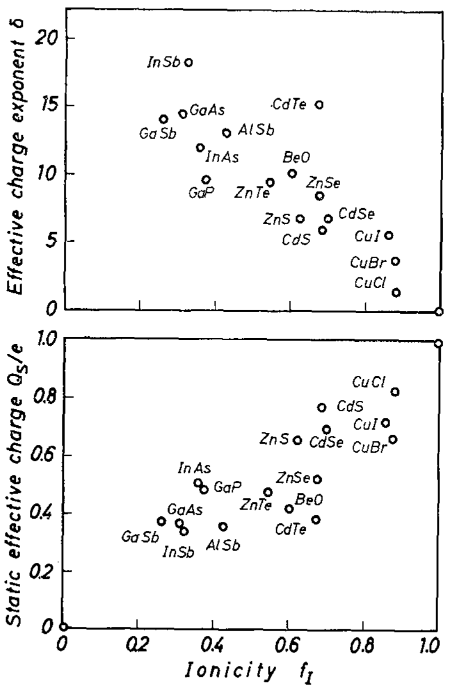

Figure 3 Correlation of bond parameters Q_S and δ with the spectroscopic ionicity [3] for various tetrahedrally co-ordinated compounds.

expects Q_S to vanish, as it is the case. The charge redistribution exponent $\delta = (\partial \ln \mu / \partial \ln r) - 1$ which is strictly not defined in the limit of purely covalent compounds, seems to reach $\delta \sim 20$ near $f_I = 0$. Of course, e_{14} and e_T still vanish in this limit because Q_S goes to zero. The overall tendency of Q_S and δ can be roughly approximated by taking Q_S as directly proportional to the ionicity f_I and δ as proportional to the covalency $(1 - f_I)$. The redistributed part $\delta \cdot Q_S$ of the dynamic charge $Q_d = -4q_d$ then shows a maximum near $f_I = 0.5$. This is reasonable since the amount of redistributed charge is expected to be largest for medium ionicity. It would be illustrative to investigate this behaviour of the static and dynamic charges by charge density calculations on the basis of pseudopotentials, similar to those performed by Walter and Cohen [17].

As for the cuprous halides, the model parameters Q_S and δ fit quite well into the systematics based on the ionicity scale. The nearby stability limit of tetrahedrally co-ordinated structures [3] does not seem to have such a marked influence on the piezoelectric behaviour as on the elastic properties [6]. On the other hand, the extreme ionicity of the cuprous halides leads to large piezoelectric coefficients. The reason for this is that the charge redistribution part of the piezoelectric coefficients is small compared to the bond bending contribution. For less ionic compounds, like for most of the II-VI compounds, the bond bending term is partly cancelled by the charge redistribution term. For the III-V compounds the charge redistribution term already dominates and the piezoelectric constants change their sign at about $f_I = 0.5$. Because Q_S is already very small in this region, the values of the piezoelectric coefficients are generally smaller than those of the cuprous halides.

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