BRIT. J. APPL. PHYS. (J. PHYS. D), 1968, SER. 2, VOL. 1. PRINTED IN GREAT BRITAIN

RESEARCH NOTES

Some measurements of isothermal compressibility by a capacitance method

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MS. received 5th July 1967

Abstract. The compressibility of some alkali halides has been measured by a fairly direct method involving a capacitance change. In order to see whether the large spread in compressibilities reported in the literature might be due to an unexpectedly large impurity effect, measurements were made on several samples of potassium chloride of differing purity; however no large impurity effect was found. A by-product of the investigations was the measurement of the variation with pressure of the dielectric constant of a hydrocarbon oil, and this showed unusual features.

1. Introduction

The compressibility of many substances has been measured by a variety of methods, which have been reviewed by Huntington (1958). The most direct methods, such as those used by Bridgman (1949), involve measuring a change in a linear dimension of a sample under hydrostatic pressure. Less direct methods involve calculation of the compressibility from other elastic constants, and in particular methods involving the speed of ultrasonic waves have received considerable attention (see e.g. Nikanorov and Stepanov 1963). While the potential accuracy of these latter methods is high, a comparison of the results so far obtained by various workers shows serious discrepancies; for example the isothermal compressibility of sodium chloride at room temperature has been quoted as low as $4{\cdot}11 \times 10^{-6}\ \mathrm{b}^{-1}$ and as high as $4{\cdot}51 \times 10^{-6}\ \mathrm{b}^{-1}$ ($1\ \mathrm{b} = 10^6$ dyn cm^{-2}). In connection with some work on the variation with pressure of the dielectric constant of the alkali halides (Jones 1967) we required to know the compressibility of the samples with an accuracy to 1% or better, and thought it advisable to make some measurements on the compressibility of the materials we were using, especially since this could be done with rather small modifications to the apparatus already available for the dielectric constant work. It is also desirable to know to what extent small amounts of impurities or defects influence the compressibility.

2. Method

The method is similar to that of Bridgman in that the sample is under hydrostatic pressure and the change in linear dimension is measured with respect to a relatively incompressible support of known compressibility. Instead of using a variable resistance or sliding fit, however, we used a capacitance change to measure the contraction. This change can be measured inside the pressure vessel with great precision, in spite of the changes in lead-through capacitance, by means of a transformer bridge (Thompson 1958). The dielectric of the capacitor is the pressure-transmitting fluid itself, a hydrocarbon oil DTD 585. This changes its dielectric constant considerably under pressure, but this effect can be allowed for by the inclusion of a second capacitor in the pressure vessel. By this means the effect on the capacitance of the change in effective area of the capacitor plates can also be eliminated. The apparatus in the pressure vessel is shown schematically in figure 1. The relatively incompressible support in the lower cell and the spacers in the upper cell are made of mild steel, which was chosen for two reasons. Firstly, as Bridgman (1949) has pointed out, the compressibility of various steels is not very different from that of iron itself. Indeed, the compressibility of mild steel as determined at the National Physical Laboratory is only 2%

higher than Bridgman's absolute determination for cast iron. Hence we may assume that the compressibility of any given sample of mild steel is probably known to well within 10%. Secondly, all materials investigated were about ten times as compressible as mild steel, except for lithium fluoride, which was about three times as compressible, and sodium fluoride, which was about five times as compressible. Hence uncertainty in the compressibility of the steel introduces systematic errors of the order of 1% for most of the alkali halides. When the effect of impurities is being studied this systematic error is irrelevant.

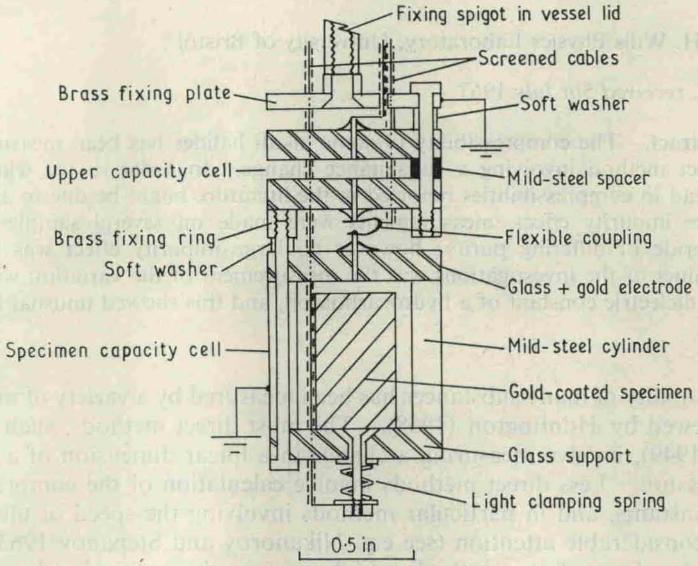

Figure 1. Compressibility cell.

Specimens were prepared by cleaving the longest possible block of crystal. The end faces were lapped flat and parallel to about 0·0002 in. A 12 BA flat-headed screw was cemented to the bottom face of the specimen with Araldite. Gold was evaporated on to all six faces of the block, which was then held down on the lowest plate glass disk by a light spring and a nut.

The two electrodes in the upper capacity cell and the upper electrode in the lower capacity cell were prepared by evaporating gold on to the glass disks, and on the two upper electrodes a central area was isolated from the rest by cutting a circular gap about 0·001 in. wide. In the case of the lower cell the central area was considerably smaller than the end face of the crystal block, and the outer annuli formed guard rings which were earthed. By combining the results from both cells the fractional change in length of the specimen is obtained in terms of the capacitance changes, various known apparatus dimensions and the compressibility of mild steel. Thus we have

$$\frac{\Delta l}{l_0}=\frac{d_0}{l_0}\left\{\left(\frac{\Delta C}{C_0}\right)_{\mathrm{u}}-\left(\frac{\Delta C}{C_0}\right)_{\mathrm{l}}-\left(\frac{\Delta C}{C_0}\right)_{\mathrm{u}}\left(\frac{\Delta C}{C_0}\right)_{\mathrm{l}}+\frac{1}{2}\left(\frac{\Delta C}{C_0}\right)_{\mathrm{l}}^2+\frac{\beta_{\mathrm{Fe}}}{3}\left(\frac{h_0}{d_0}-1\right)\Delta P\right\}$$

where l_0, h_0, d_0 are the zero-pressure lengths of the specimen, mild-steel support and mild-steel spacers respectively, Δl is the change in specimen length corresponding to a pressure ΔP above zero pressure, $(\Delta C/C_0)_{\mathrm{u}}$ and $(\Delta C/C_0)_{\mathrm{l}}$ are the fractional capacitance changes in the upper and lower cells at a pressure ΔP, and β_{Fe} is the compressibility of mild steel. The value used for β_{Fe} was $0{\cdot}595\times10^{-6}\ \mathrm{b}^{-1}$ (Kaye and Laby 1966, p. 33).

The capacitance measurements were made with a Wayne Kerr B921 bridge operating at 1 kHz.

3. Results

The upper curve of figure 2 shows $\Delta l/l_0$ for a specimen of KCl, and the lower curve that for a specimen of LiF. The two curves in figure 3 show the fractional change in dielectric constant of the DTD 585 oil in the upper cell. In order to obtain this result from the change in capacitance of the upper cell a value of $4{\cdot}8\times10^{-6}\ \mathrm{b}^{-1}$ for the compressibility of plate glass was assumed (Bridgman 1929). The compressibilities of the alkali halides are of course independent of this assumption. The results for DTD 585 oil are presented because of the very unusual way in which the dielectric constant changes as compared with many other organic liquids (Danforth 1931, Scaife 1955, Gilchrist *et al.* 1957). The fact that the measured compressibilities of the halides show no comparable anomaly gives us confidence that the result is not an instrumental artefact. The change in volume with pressure of DTD 585 oil shows no plateau (Bingham 1955), so the anomaly is a polarization anomaly entirely. In a qualitative manner we can say that as the pressure rises the dominant effect initially is the increase in the number of polarizable particles per unit volume, which produces an increase in the dielectric constant. At 20°c and 4 kb the inhibiting effects of neighbours on the polarizability of each molecule just offsets the rate of increase of density, and a plateau occurs. However, as the pressure is increased further the dielectric constant unexpectedly begins to rise again. Perhaps some change in molecular structure occurs such that the polarizability is reduced.

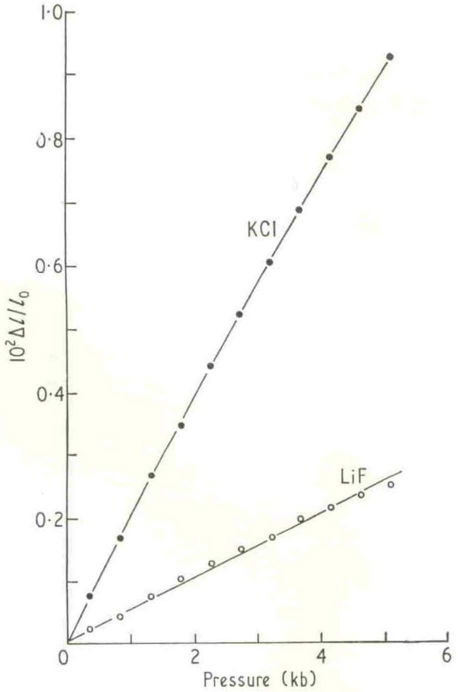

Figure 2. A sample of compressibility cell results.

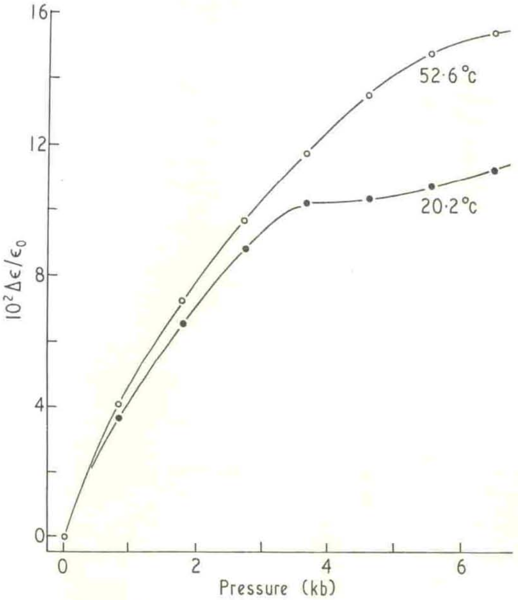

Figure 3. Variation of the dielectric constant of DTD 585 oil with pressure.

The table contains the results and impurity analyses of all substances from which sufficiently large pieces of single crystal could be cut. The divalent ion concentrations have been determined from ionic conductivity measurements, the hydroxyl ion concentrations (the most likely anionic impurity) from ultra-violet and infra-red absorption, and the dislocation content by etching.

The best values of the coefficients a and b in the expression

$$\Delta V/V_0=-a\Delta P+b(\Delta P)^2$$

The compressibility of some ionic solids of varying purity†

nce	Divalent ions (p.p.m.)	Dislocations $(10^{6}\ \mathrm{cm}^{-2})$	OH^{-} ions $(10^{16}\ \mathrm{cm}^{-3})$	Temp. (°c)	$10^{6}a$ (b^{-1})	$10^{12}b$ (b^{-2})
	—	—	10^{2}	16·5	—	—
	—	—	—	20·0	—	—
i)	0·7	—	—	17·0	—	—
				50·0	—	—
ii)	6	—	—	18·9	—	—
				54·6	—	—
i)	0·3	0·2	3	18·0	5·94±0·10	100±15
ed)				53·1	6·13±0·05	85±9
ii)	10	10	<5	15·6	5·90±0·08	93±15
				57·1	6·10±0·05	80±8
iii)	0·8	0·5	10	18·0	—	—
				52·6	—	—
iv)	0·8	5	≪1	20·0	—	—
				30·0	—	—
v)	300	0·5	10	20·5	5·88±0·06	98±9
				20·2	5·89±0·08	102±12
				52·6	6·16±0·11	117±15
i)	—	—	—	22·0	8·58±0·06	240±20
·5%)				35·0	8·64±0·08	200±20
	—	—	—	19·5	6·51±0·03	82±4
				44·0	6·70±0·04	95±8
	—	—	—	18·0	7·19±0·05	124±8
				51·4	7·28±0·15	102±32

table imply that a quantity has not been measured.

where V is the crystal volume, have been determined, together with their standard deviations. In some cases, due to the shortness ($\lesssim 1$ cm) of the largest specimen available, only an average value of a can be used, namely

$$a' = \frac{1}{V_0}\left(\frac{\Delta V}{\Delta P}\right)_T \qquad \text{at 7 kb}$$

and b values are unreliable. For the sake of comparison some values of a' are quoted in the table in cases where this restriction does not apply. It is felt that if a longer pressure vessel were built and longer specimens of the more compressible alkali halides were obtained (~ 5 cm) then it should be possible to achieve accuracies of about 0·1% in the value of a and 1% in the value of b using this technique.

The results obtained with the different specimens of potassium chloride show that trace impurities do not have disproportionate effects on the compressibility. Thus is it unlikely that differences in the purity of the specimens used can account for more than a small part of the spread in the results obtained by various authors. The results obtained here for the values of a and b lie within the range defined by previous workers in every case.

Acknowledgments

We would like to thank Dr. J. Parry and Mr. W. G. Windsor of the Mechanical Engineering Department, University of Bristol, for assistance in calibrating the manganin gauge used to measure the pressure, and Dr. D. Pooley of Harwell for some NaCl and KI specimens.

One of us (B.W.J.) would like to thank the Science Research Council for the award of a grant.

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