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Elastic Constants of LiF from 4.2°K to 300°K by Ultrasonic Methods*

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The values of the elastic constants of LiF at 4.2°K are found to be $c_{11}=12.46\times10^{11}$, $c_{44}=6.49\times10^{11}$, and $c_{12}=4.24\times10^{11}$ dynes/cm². At 300°K $c_{11}=11.12\times10^{11}$, $c_{44}=6.28\times10^{11}$, and $c_{12}=4.20\times10^{11}$ dynes/cm². A Debye characteristic temperature, θ_D, has been calculated from these values by using the Houston method of averaging the velocity over different directions in the crystal. At 4.2°K, $\theta_D=734$°K in good agreement with the specific heat work of Martin. At 300°K, $\theta_D=708$°K which is not in good agreement with values derived from specific heat measurements. A model has been suggested in which a combination of Debye and Einstein terms is used in the specific heat theory.

INTRODUCTION

An investigation of the elastic constants of single crystals of LiF has been undertaken for the purpose of giving needed fundamental information in solid state physics. For example, Löwdin[1] has calculated theoretical values for c_{44}, c_{12}, and the compressibility at the absolute zero of temperature which we may now compare with our new results. The elastic constants may be used in computation of the frequency spectrum of lattice vibrations.[2] More simply, of course, the velocity of longitudinal and of transverse waves may be used to compute the Debye characteristic temperature, θ_D, and the values may be compared with the experimentally derived θ_D from specific heat measurements.[3,4] Finally, we are interested in detailed knowledge of the lattice-vibration spectrum for purposes of understanding nuclear magnetic resonance studies on relaxation effects and line shape.

EXPERIMENTAL

The experimental apparatus was essentially the same as that used by Overton and Swim[5] in this laboratory and very similar to that described in more detail by Huntington.[6] The echo ranging technique was used to determine the velocity of longitudinal and transverse 10-megacycle waves along specific directions in the LiF single-crystal specimens. It has been experimentally established that in order to obtain well-defined echoes it is necessary to have the quartz-crystal transducer physically bonded to the specimen in some manner. As the temperature is lowered, a problem occurs since the differential thermal contraction between the specimen, the binding agent, and the quartz crystal may result in the breakage of any one of the three. For the temperature range 4.2°K to 200°K a Dow Corning Silicone Adhesive XC-270 was found to work very well if the temperature of the specimen was lowered at a rate of 10°K per hour or less. Measurements above 200°K were made using stopcock grease and beeswax as binding agents. There is very little attenuation of the pressure waves in LiF and we could see 75 or more return echoes on the 1000-μsec sweep of the DuMont 256 scope. We are studying the attenuation as a continuing problem, particularly at very low temperatures and under conditions of nuclear-spin precession frequencies equal to the frequency of our pressure waves.

The optically clear single crystals of LiF used in this investigation were obtained from the Harshaw Chemical Company. One specimen was of dimensions 3 in.×1 in.×1 in. with the 1-inch square face perpendicular to the (100) plane while the other specimen was $1\frac{1}{2}$ in.×1 in.×1 in. with 1-inch square face perpendicular to the (110) plane. It was necessary to polish the 1-inch square faces so that they were both flat and parallel to each other.

RESULTS

The velocities shown in Table I were calculated from measurements of the time between successive echoes and the length of the specimen. From these velocities the three independent elastic constants of the cubic crystal were computed by using the following expressions, where ρ is the density of the specimen and v is the velocity of the particular type wave used:

(1) a longitudinal wave with the direction of propagation perpendicular to the (100) plane $\rho v^2=c_{11}$,

(2) a transverse wave with the direction of propagation perpendicular to the (100) plane $\rho v^2=c_{44}$,

(3) a longitudinal wave with the direction of propagation perpendicular to the (110) plane $\rho v^2=\frac{1}{2}(c_{11}+c_{12}+2c_{44})$.

In Table II our data are compared with the experimental work of Huntington[6] and of Bergmann[7] at room temperature and with the theoretical calculations

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[2] J. DeLaunay, in *Solid State Physics* (Academic Press, Inc., New York, 1956), Vol. 2.

[3] Clusius, Goldman, and Perlick, Z. Naturforsch. A4, 424 (1949).

[4] D. L. Martin, Phil. Mag. 46, 751 (1955).

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[6] H. B. Huntington Phys. Rev. 72, 321 (1947).

[7] L. Bergmann, *Ultrasonics and Their Scientific and Technical Applications* (J. W. Edwards, Ann Arbor, 1944), p. 332.

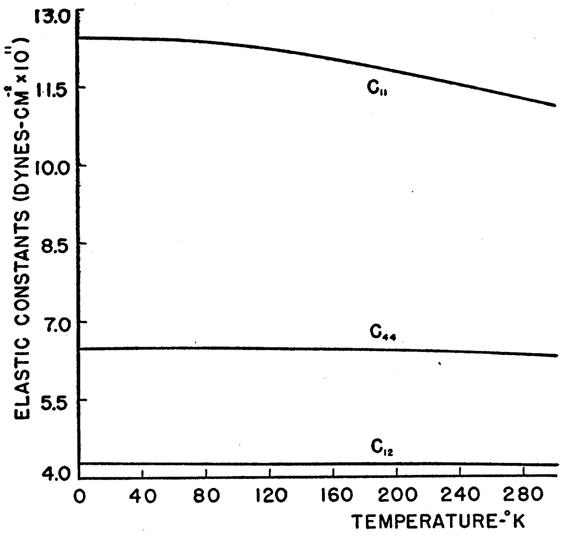

FIG. 1. Elastic constants of LiF as a function of temperature.

of Löwdin[1] for the absolute zero of temperature. A plot of the three elastic constants *vs* temperature is given in Fig. 1. The variation from room temperature to 4.2°K of c_{11} and c_{44} is seen to be about 12% and 3%, respectively, while c_{12} is practically independent of temperature since its variation is less than 1%. In making the preceding calculations the data of Adenstedt[8] on linear expansion as a function of temperature were used in correcting for the change in the length and density of the LiF specimens as the temperature was lowered.

The compressibility β can be calculated from the elastic constants by using the following expression[9]:

$$\beta = 3/(c_{11}+2c_{12}).$$

When one uses the values of c_{11} and c_{12} obtained from Fig. 1, the value of β is computed to be 1.54×10^{-12} cm²/dyne at room temperature and 1.43×10^{-12} cm²/dyne at 4.2°K. Slater[10] gives an experimental value of 1.53×10^{-12} cm²/dyne for β at room temperature, and by an extrapolation estimates it to be 1.4×10^{-12} cm²/dyne at $T=0$°K. According to the theoretical calculation of Löwdin,[1] $\beta=1.3\times10^{-12}$ cm²/dyne at $T=0$°K. The temperature variation of the compressibility modulus, $K=1/\beta$, of LiF is seen to be quite similar to that of KBr as deduced by Kittel[11] from the experimental work of Galt.[12] Kittel showed that this dependence of K on temperature could be accounted for by considering the theory of anharmonic lattice dynamics as formulated by Debye.[13]

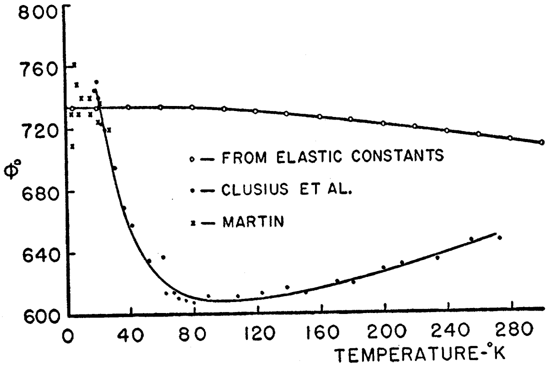

FIG. 2. Debye characteristic temperature, θ_D, of LiF from various sources as a function of temperature.

DISCUSSION

In the Debye[14] theory of specific heat of solids the medium is considered to be an isotropic elastic continuum and the frequency distribution arising from the standing waves gives the number of normal modes between ν and $\nu+d\nu$ as

$$f(\nu)d\nu = 3V(4\pi/v^3)\nu^2 d\nu, \tag{1}$$

where V is the volume of the specimen and v is the velocity of sound. If there are $3N$ degrees of freedom, we must have an upper limit to the integral of this expression, and this leads to the well-known maximum frequency given by

$$\nu_{\max} = (3s/4\pi\Delta)^{\frac{1}{3}}v, \tag{2}$$

TABLE I. Ultrasonic velocities in LiF as a function of temperature. $V_L(100)$ = velocity in meters/sec of longitudinal wave propagated in the (100) direction. $V_T(100)$ = velocity in meters/sec of transverse wave propagated in (100) direction. $V_L(110)$ = velocity in meters/sec of longitudinal wave propagated in (110) direction.

T°K	V_L (100) ±0.5%	V_T (100) ±0.5%	V_L (110) ±0.5%	θ_D °K	Compressibility in units 10^{-12} cm²/dyne
4.2	6866	4951	7494	734	1.43
20	6866	4951	7494	734	1.43
40	6862	4951	7486	734	1.43
60	6855	4951	7483	734	1.43
80	6844	4951	7476	733	1.44
100	6827	4951	7470	732	1.44
120	6804	4951	7460	730	1.45
140	6778	4950	7449	728	1.46
160	6750	4950	7438	726	1.47
180	6722	4949	7426	724	1.48
200	6692	4947	7415	721	1.49
220	6661	4943	7400	719	1.50
240	6630	4938	7382	716	1.51
260	6599	4932	7365	714	1.52
280	6567	4926	7344	711	1.53
300	6536	4920	7325	708	1.54

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[14] P. Debye, Ann. Physik **39**, 789 (1912).

where s is the number of atoms per cell, Δ is the cell volume, and v is the velocity of lattice waves (taken equal to the velocity of sound). At very low temperatures and for a monotomic solid made up of an Avogadro number of atoms, the well-known expression for the specific heat is

$$C_v = 464.5(T/\theta_D)^3 \text{ cal/(°K) (g atom)}, \qquad (3)$$

where $\theta_D = h\nu_{\max}/k$ is the characteristic temperature computed from the measured sound velocity in the medium by use of the above equations.

In a cubic crystal such as LiF, which is not isotropic [the ratio $2c_{44}/(c_{11}-c_{12}) = 1.58$], the observed velocity does depend on the direction of propagation through the crystal. In order to obtain a meaningful value for the θ_D, the velocity must in some manner be averaged over the different directions in the crystal. The method proposed by Houston[15] was used to calculate an average θ_D from the measured elastic constants and the results are given in Table I. Actually we followed the procedure of Betts *et al.*,[16] in which the velocity was averaged over six directions in the LiF crystal.

Figure 2 shows the computed value of θ_D as a function of temperature as listed in Table I, and also shows the values of Clusius *et al.*[3] and of Martin[4] which they have deduced by comparing the simple Debye theory to their experimental results. The agreement is good at very low temperatures. We would emphasize that the averaging process is quite important because, for example, using the velocities of waves moving perpendicular to the (100) plane we get $\theta_D = 787$°K at very low temperatures, and this is clearly not valid.

In Fig. 3 the experimental specific heat from the work of Clusius *et al.*[3] and of Martin[4] is plotted. The specific heat calculated from the simple Debye theory, with our value of θ_D, is shown on the plot and gives a poor fit indeed at temperatures above 20°K. In an attempt to throw light on the kind of frequency spectrum needed for better agreement, the following scheme was used to calculate the specific heat. In the face-centered cubic lattice structure of LiF the small Li ion (radius 0.60 A) occupies a sort of cell surrounded by the larger F ions (radius 1.36A). The large ions nearly touch all around and strongly repel one another. If one assumes that the Li ions behave as a set of Einstein oscillators and that the F ions obey a Debye distribution function, the expression for the specific heat per mole of LiF then becomes

$$C_v = 3RF_D(\theta_D/T) + 3RF_E(\theta_E/T).$$

The value of $\theta_E = h\nu/k$ is computed from the frequency, ν, taken from the infrared absorption[16] as 9.2×10^{12} cycles/sec. However, the θ_D was taken to be 580°K, which is different from the values listed in Table I, because our model insists that the fluorine ion occupies the entire volume to be used in the calculation of Eq. (2). The results of the calculation are also shown on Fig. 3. Obviously, only a true vibration spectrum can give the correct result. If there is an element of truth in our model, then such a theory should be even more valid for the salts LiCl, LiBr, and LiI, where the anions are even larger and the Li ion is indeed left in a pocket where it may behave as a simple oscillator.

TABLE II. Elastic constants of LiF in units of 10^{11} dynes/cm^2. The values quoted here due to Huntington have been corrected by using the known value of 2.601 g/cc for the density of LiF at room temperature. In his paper Huntington reported using a value of 2.295 g/cc obtained from the *Handbook of Chemistry and Physics*, which is incorrect.

Elastic constant 10^{11} dynes/cm^2	Huntington $T \cong 300$°K	Bergmann $T \cong 300$°K	Löwdin $T = 0$°K	Present experimental work $T = 300$°K	$T = 0$°K
c_{11}	11.07	11.77		11.12	12.46
c_{44}	6.28	6.28	5.544	6.28	6.49
c_{12}	4.57	4.33	4.044	4.20	4.24

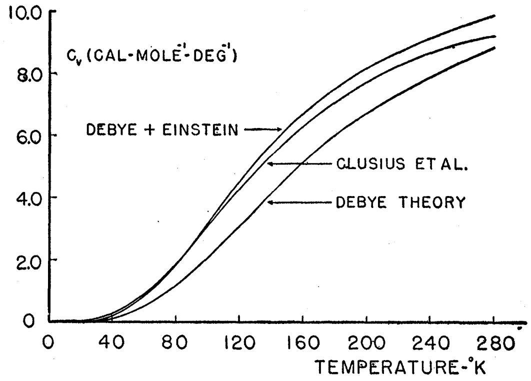

FIG. 3. Experimental and calculated specific heat of LiF as a function of temperature.

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[16] Betts, Bhatia, and Wyman, Phys. Rev. **104**, 37 (1957).