Elastic constants of single-crystal lithium indium

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The elastic constants of single-crystal lithium indium (NaTl type: space group $Fd\,3\,m$) were determined at room temperature by an ultrasonic pulse-transmission technique. The values of the elastic constants, in units of 10^{11} dyn/cm^2, are: $c_{11} = 5.589$, $C_{12} = 4.169$, and $C_{44} = 2.666$. The results give deviation from Born-Smith dynamic lattice theory if nearest-neighbor interactions alone are considered. The binding force of LiIn is discussed. The value of the Debye temperature is also determined by using de Launay's tables to be 211.2°K.

I. INTRODUCTION

The binary LiM (M = Al, Ga and In) intermetallic compounds are known to crystallize in the NaTl structure (space group $Fd3m$, Fig. 1) using x-ray powder diffraction.[1,2] Recently, one of the authors obtained data definitely confirming the NaTl structure for LiAl by neutron diffraction.[3] The NaTl structure is composed of two sublattices, each forming a diamond lattice and interpenetrating each other. If the Na atom gives up its single valency electron to the more electronegative Tl atom, the Tl atom has four electrons to form a diamond substructure using sp^3 orbitals.[4] Therefore, it will be either a narrow-gap semiconductor or a semimetal with low carrier concentration.[5-7] The mechanical properties of these materials are expected to differ from the diamond or the zinc-blende structure because each atom of the NaTl structure has eight nearest neighbors, four like and four unlike, although the crystal class of LiIn is $Fd\,3m$ as for the diamond structure. The measurements of the elastic constants provide information about mechanical or thermodynamic properties of the lattice.

II. EXPERIMENTAL

Lithium indium is a cubic crystal, and thus it has the independent elastic constants: C_{11}, C_{12}, and C_{44}. The elastic stiffness constants were determined by measuring[8] the sound velocity in different crystalline directions, by an ultrasonic pulse-transmission method, utilizing rectified pulses at 450 Hz. The block diagram of the system used in the present investigation is shown in Fig. 2.

The pulse generator is similar to a 450-Hz multivibrator, and its output is converted into the shot pulses through the rectified and the differentiation circuit. These pulses proceed to the transmitting quartz crystal, traverse the acoustic path, are picked up by the receiving quartz crystal, and amplified by the wide-band amplifier. The amplified output is impressed across the vertical plates of the cathode-ray oscilloscope. On the other hand, the output of the basic oscillator is applied the horizontal plates of the oscilloscope through the variable delay circuit. In this system, the limit of the measurement of the change in transit time is 0.01 μsec. The accuracy was confirmed by tests made on aluminum samples of several different lengths.

Single crystals of LiIn of sufficient size (about 1 cm in length and 1.10 cm in diameter) for ultrasonic measurement were grown by the Bridgman technique.[9] These crystals were oriented by means of x-ray Laue back reflection, and two pairs of parallel surfaces were ground on it. One set of surfaces corresponded to a (001) crystalline plane, while the other set corresponded to a (110) plane. The distances between parallel faces measured

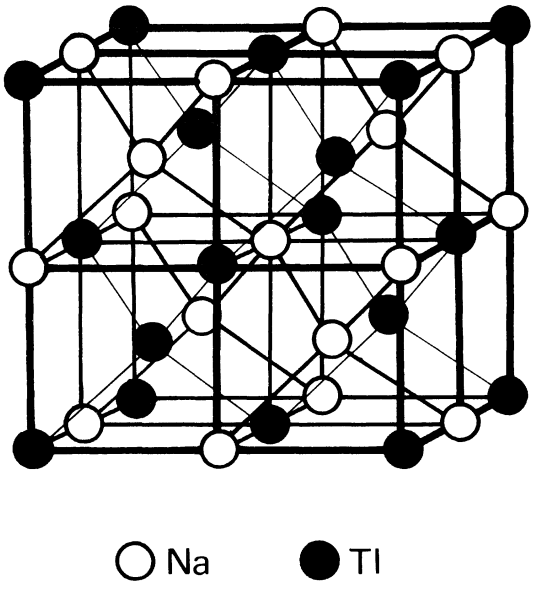

FIG. 1. NaTl structure. Each Na atom has four Na and four Tl near neighbors and six Tl next-near neighbors. The space group is $Fd3m$.

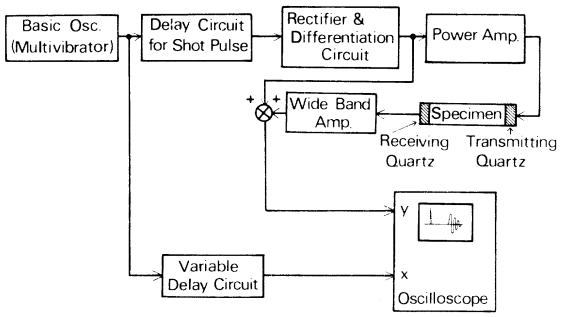

FIG. 2. Block diagram for ultrasonic measurement.

with a calibrated micrometer were 0.7699 cm in the [001] direction and 0.7261 cm in the [110] direction.

The room-temperature density of LiIn was taken to be 5.158 g cm^{-3}. This value was calculated from the lattice parameter determined by x-ray measurements.[9]

X cut and *Y* cut 1-MHz quartz transducers 0.8 cm in diameter and gold plated on both sides were employed to generate longitudinal and shear acoustic waves, respectively. The binder between the sample and the quartz transducer was a paraffin oil or an electron wax.

III. RESULTS AND DISCUSSION

Two LiIn crystals were used during this investigation. These samples were designated LiIn *A* and *B*, respectively.

The transit time of the pure longitudinal and transverse wave propagating in the [001] and [110] direction were measured at room temperature. In order to examine the effect of interference between the incident and reflected wave, a one-shot pulse was transmitted to the crystal. However, the effect was not clearly observed in this method. Table I has pertinent data on these crystals for room temperature. These values were confirmed by a good many measurements.

If each atom of a crystal is at an inversion center and interacts other atoms with central forces, the Cauchy relations[10] must exist between the elastic constants. For a cubic crystal, there is only one Cauchy relation, namely

$$C_{12} = C_{44}.$$

An inspection of Table I shows that this relation is not satisfied. When the relations between the stiffness constants deviate from the Cauchy relations, one cannot conclude immediately that the forces are noncentral. However, since each atom of the NaTl type structure is at an inversion center as in the case of the diamond type structure, we may say that the forces between atoms are the covalent binding forces rather than the central forces. Other evidence[5] for the covalency of the NaTl structure is as follows. There are 8 group-I atoms and 8 group-III atoms in a unit cell, so that we have 32 states, (including spin) and 32 electrons (8 from I and 24 from III), i.e., the group-I atoms form an *s*-like band far below the Fermi surface and the group-III atoms supply *s* and *p* electrons to fill up the band. A model which assumes only central force interactions would be unsatisfactory, according to these evidences.

The first model of the diamond structure has been worked out by Born[11] and developed further by Smith.[12] It is a two-constant model dealing with nearest-neighbor interactions alone. One force constant is associated with the radial force and the other with the angular force. Smith extended Born's treatment to a three-constant model by including next-nearest neighbors interacting under central forces.

According to Born-Smith dynamic lattice theory, the elastic constants are related by the expression

TABLE I. Sound velocity and elastic constants of LiIn measured at room temperature.

Sample	Length (cm)	v_s (long.) (10^5 cm/sec)	v_s (trans.)
A (011)	0.7261	3.825	
B (001)	0.7699	3.292	2.274

Elastic stiffness constant (10^{11} dyn/cm^2)	C_{11}	C_{12}	C_{44}
	5.589	4.169	2.666

Elastic compliance constant (10^{-12} cm^2/dyn)	S_{11}	S_{12}	S_{44}
	4.934	−2.107	3.750

Mean bulk modulus	4.643×10^{11} dyn/cm^2
Mean shear modulus	1.576×10^{11} dyn/cm^2
Mean Young's modulus	3.875×10^{11} dyn/cm^2
Anisotropy factor	3.76

TABLE II. Comparison of results of first-neighbor forces lattice theory.

	Si	Ge	InSb	ZnS	LiIn
$4C_{11}(C_{11}-C_{44})/(C_{11}+C_{12})^2$	0.99[a]	1.02[b]	0.94[c]	0.89[d]	0.69

[a]H. J. McSkimin, J. Appl. Phys. 24, 988 (1953).
[b]M. E. Fine, J. Appl. Phys. 26, 862 (1955).
[c]R. F. Potter, Phys. Rev. 103, 47 (1956).
[d]R. J. Collins and H. Y. Fan, Phys. Rev. 93, 676 (1954).

TABLE III. Results of using various methods to calculate the Debye temperature of LiIn.

Method	Θ of LiIn
Table (de Launay)	211.2 °K
Graph (Marcus)	210.0 °K
Power-series expansion	211.0 °K
Graph (Leibfried)	210.3 °K
Kubic harmonic expansion	212.3 °K
Voight-Reuss-Hill techniques	217.0 °K

$$4C_{11}(C_{11}-C_{44})/(C_{11}+C_{12})^2=1\ .$$

Table II shows for comparison purposes the results for Si, Ge, InSb, ZnS, and LiIn using this theory. The element or intermetallic compound semiconductors with a strong covalent bond satisfy the Born relation. Although the space group of the NaTl structure is $Fd3m$ as well as the diamond structure, the departure from the theory may be explained from the fact that each atom of the NaTl structure has eight nearest neighbors, four like and four unlike. The binding force of LiIn may be constituted of the In-Li bond which is associated with the ionic binding force in addition to the In-In bond related to the covalent binding. Furthermore, the weak metallic bond may exist between lithium and indium atom or lithium and lithium atom. However, *Ia-IIIb* intermetallic compounds with the NaTl structure except NaTl are essentially nonmagnetic,[13,14] i.e., their susceptibilities, after the subtraction of core diamagnetism, are essentially zero. In the NMR experiment[15] of these compounds, the size of the quadrupole interaction is consistent with a high degree of covalency in these crystals. Other evidence[16] of the deviation from a metallic bond is that the atomic radii ($r_{Li}=r_{In}=1.47$ Å) in LiIn are smaller than the metallic radii ($r_{Li}=r_{In}=1.52$ Å), namely the contraction between atoms is 3.3%. And then these compounds contain a 2.7% vacancy concentration[15] in the lithium sublattice between 77 and 100 °K, i.e., they have the defect lattices. On the other hand, the elastic constants are scarcely dependent on the vacancies.[17] We assume that the cause of the metallic conductivity[18] of LiIn may be found by the large vacancy concentrations and In-Li and Li-Li bond which is associated with the metallic bond. However, the contribution of these weak In-Li and Li-Li bonds must be concealed by the influence of a high degree of vacancy concentration.

The Debye temperature is an important parameter of a solid. The Debye temperature can be easily calculated from the elastic moduli using various methods[19,20] such as the one based on the de Launay's tables, the graphical methods proposed by Marcus and by Leibfried, the power-series expansion due to Sutton, the Kubic harmonic expansion, and the Voigt-Reuss-Hill techniques. Table III gives the results obtained by the various methods for LiIn crystal. In the process of the method due to Sutton,[21] the mean velocity of sound is calculated to be $v_m=1.91\times10^5$ cm/sec.

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