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The Variation of the Elastic Constants of Lithium with Temperature and Pressure

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The elastic constants $C' = (C_{11} - C_{12})/2$, C_{11}^S and $C_n^S = C_{11}^S - C' + C_{44}$ of lithium single crystals were measured in the temperature interval 85 to 300 °K and the pressure interval 0.001 to 3.5 kbar. Of special interest is the behavior of C' near the martensitic transformation (which at 1 bar occurs near 78 °K) to determine the applicability of either a bulk or a microscopic instability criteria to the transformation. A pulsed ultrasonic interferometer was employed to measure the transit times of the lithium samples from which the elastic constants were calculated. The resulting data indicate that the elastic constants do not change in any drastic manner and are continuously increasing as the temperature is lowered. In addition, all pressure derivatives remain positive to the lowest temperatures and highest pressures studied. Comparisons of the presently reported quantities with those previously measured and theoretically calculated are made.

Die elastischen Konstanten $C' = (C_{11} - C_{12})/2$, C_{11}^S und $C_n^S = C_{11}^S - C' + C_{44}$ von Lithium-Einkristallen wurden im Temperaturbereich von 85 bis 300 °K und im Druckintervall von 0,001 bis 3,5 kbar gemessen. Von besonderem Interesse ist das Verhalten von C' in der Nähe des Martensitübergangs (der bei 1 bar in der Nähe von 78 °K auftritt), um die Anwendbarkeit von entweder Volumen- oder mikroskopischen Instabilitätskriterien für den Übergang zu bestimmen. Für die Messung der Übergangszeit der Lithiumproben, von denen die elastischen Konstanten berechnet wurden, wurde ein Ultraschall-Impulsinterferometer benutzt. Die erhaltenen Ergebnisse zeigen, daß die elastischen Konstanten sich in keiner Weise drastisch ändern und daß sie kontinuierlich ansteigen, wenn die Temperatur erniedrigt wird. Darüber hinaus bleiben alle Druckableitungen positiv bis zu den niedrigsten untersuchten Temperaturen und höchsten Drücken. Es wird ein Vergleich der publizierten Werte mit früher gemessenen und theoretisch berechneten durchgeführt.

1. Introduction

In this introduction we discuss, in order, the martensitic transformation in lithium, the bulk elastic instability criteria, Zener's proposed mechanism, and an elastic instability criteria applicable to "bad" crystal material such as dislocations. Finally, we briefly discuss the calculation of elastic constants.

1.1 Martensite transformation

As a result of investigations into the physical properties of the alkali metals at low temperatures, lithium and sodium were found to undergo martensitic-type structural transformations at 78 and 35 °K, respectively [1 to 3]. No transformation was observed in potassium, rubidium, or cesium [2, 4]. Further X-ray research [4] revealed that the high temperature body-centered cubic (b.c.c.) structures of lithium and sodium transformed, upon cooling through the transformation temperature (M_S), to highly faulted hexagonal closed-packed (h.c.p.)

structures with a nearly ideal *c–a* ratio. Upon cold working at temperatures below M_S, lithium was found to undergo yet another transformation to a faulted face-centered cubic (f.c.c.) structure [1, 4, 5].

Gugan and Dugdale [6] determined the pressure variation of M_S to be +25 °K/kbar to 2 kbar pressure, thus indicating that hydrostatic pressure affects transformation characteristics. The purpose of this research was to investigate the variation of the elastic constants of lithium¹) near (but above) M_S as a function of pressure. Of particular interest were derivatives of C', namely $\mathrm{d}C'/\mathrm{d}T$ at pressure, to determine the applicability of the bulk elastic instability hypothesis originally postulated by Zener [7, 8], and $\mathrm{d}C'/\mathrm{d}P$ at temperatures near M_S, to test a microscopic elastic instability hypothesis discussed herein.

The martensitic transformation is a solid state phenomenon which does not necessarily involve diffusion, but appears to involve many thousands of atoms which move cooperatively with a velocity of the same order as the velocity of sound in the crystal. The lithium transformation is in many respects similar to the characteristic transformation discussed in detail in the literature [9 to 17]. Of the 7 characteristics listed by Christian [17], only the stipulation of reversibility does not apply to lithium; that is, when a crystal is reconverted from low-temperature phase to high-temperature phase, in the case of lithium the original shape and orientation are not regained. When this type of behaviour has been observed in iron alloys, it is usually attributable to the presence of a higher concentration of the alloying element at the grain boundaries. This segregation effects a pinning of the boundaries which do not recede when the temperature is raised. The boundaries then exist although the material within them has transformed to the original phase.

1.2 Macroscopic elastic instability

The strain energy of a crystal is positive for any small deformation if the elastic constant matrix is positive definite. For a cubic crystal this reduces to $C_{44} > 0$, $C' > 0$, $C_{11} > 0$, and $B > 0$. Should any one of these relations not be satisfied, the crystal is said to have a macroscopic elastic instability. Thus if $C' < 0$, a (110) [1$\bar{1}$0] shear would spontaneously occur. Zener [7, 8] suggested that such a situation was likely in certain b.c.c. metals, e.g. β-brass. In the alkali metals $C' \ll C_{44}$ at room temperature [9]; moreover lithium and sodium do transform to closest packed structures.

1.3 Microscopic elastic instability

It is clear from the work of others [18, 19] and the present work that no macroscopic instability exists at atmospheric pressure at the transformation temperature (including temperatures above and below). It is, however, conceivable that in regions of the solid where the packing is not characteristic of the perfect b.c.c. crystal and in which additional stress may be present, elastic instabilities may exist. (An example of such a region is a grain boundary.) We call this an

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¹) All elastic constants shown herein are adiabatic unless otherwise indicated. The adiabatic and isothermal values of the shear constants are equal while longitudinal wave constants are not. Thus C_{11} (longitudinal constant in 100 direction), B (bulk modulus) and C_n (longitudinal constant in 110 direction) have either T (isothermal) or S (adiabatic) superscript, the S superscript implied if none is written.

imperfection elastic instability. When the crystal is cooled to below the equilibrium transformation temperature, these regions (which were previously transformed) propagate through the crystal, transforming the entire crystal to the closest packed phase. As an example, consider the core of a dislocation. Usually there is a dilatation of two atomic volumes per atom length of dislocation. A crude model assumes that linear elasticity describes the stress field of the dislocation which is postulated to be hollow. The stress field arises from the rigid displacement and the presence of an internal pressure P in the cylindrical core. If $P \approx B/6$, this model leads to the expected dilatation. For lithium the quantity $B/6$ represents a pressure of approximately 22 kbar. Although C' at $P = 0$ is not zero, there exists the possibility that $\mathrm{d}C'/\mathrm{d}P$ is negative so that C' might in fact be zero at the pressure assumed to be present in the core.

1.4 Theoretical predictions of elastic constants

The pioneering work in the area of calculating the elastic properties of metals was performed in the mid-thirties by Wigner and Seitz [20 to 22], Bardeen [23] and Fuchs [24]. The latter approach yielded elastic constants other than the bulk modulus, and has been varied [25 to 28] to explain discrepancies between observed and calculated data. Since the mid-sixties an approach applying pseudopotential theory [29 to 32] has enabled theorists to calculate various properties, including the elastic constants, of the simple metals and to predict elastic constant values which agree well with recently reported experimental results.

In the present paper results are presented which show that a bulk instability does not exist. Moreover, the present evidence tends to rule out the imperfection elastic instability mechanism (but not completely). Finally, we show that the agreement between the measured pressure derivatives and theoretically predicted values at 0 °K is fair.

2. Experimental Techniques

A pulsed ultrasonic interferometer was used to measure the elastic constants of the lithium single crystals. The pulse system is described in detail elsewhere [33], as are the temperature and pressure control systems [34].

The scarcity of single crystal data on lithium metal is primarily due to the difficulty of obtaining large single crystals. Bender [35] made unsuccessful attempts to grow lithium single crystals although he was able to obtain large single crystals of both sodium and potassium. Bowers et al. [36] reported a successful method for producing small (0.63 cm diameter) cylindrical single crystals. The procedure originated by Nash and Smith [18] was used to produce the crystals for the present research.

The ultrasonic specimen preparation for lithium follows those procedures for sodium outlined by Martinson [33]. The etching and cleaning solutions used were anhydrous diethyl-ether and methyl alcohol, respectively. The final sample size was approximately $(1.5 \times 1.0 \times 1.0)$ cm^3.

3. Data Analysis

The analysis of the results of the experiments (frequencies at sets of T, P) was carried out in the following manner:

1. The transit times were corrected to take into account the presence of a transducer.

2. The length l_0 at temperature T and atmospheric pressure was computed from thermal expansion data.

3. The length l at T, P was computed as described later.

4. A least square analysis was then used at each temperature with C having the linear form

$$C = C|_{P=0,\,T} + \left.\frac{\mathrm{d}C}{\mathrm{d}P}\right|_{P=0,\,T} P\,. \tag{1}$$

The equation for the transit time is

$$2\tau = \frac{n - \frac{1}{2} + p}{f_n p} + k(f_n^{-1} - f_0^{-1})\,, \tag{2}$$

where 2τ is the round trip transit time of the sample, f_n is the frequency at which interference occurs, n is an integer associated with the frequency f_n, p is the difference between the number of round trips of the two pulses, k is the ratio of the transducer to sample acoustic impedances, and f_0 is the free resonance frequency of the transducer. The elastic constant is calculated from the following formula:

$$C = \varrho \frac{l^2}{\tau^2}, \tag{3}$$

where ϱ and l are the sample density and length, respectively. The temperature and pressure variation of the resonance frequency of the transducer are taken from McSkimin and Andreatch [37] and the length change variation of the lithium sample with temperature is from Pearson [38]. Cook's analysis [39] was used to evaluate the length change of the sample resulting from the application of hydrostatic pressure. This involved the calculation of the conversion factor Δ at temperature and pressure. The specific heat data of Martin [40] was used in addition to Pearson's data to calculate Δ as defined by

$$\Delta = \frac{\beta^2 B^S T}{\varrho C_P}, \tag{4}$$

where β is the volume thermal expansion coefficient, C_P is the heat capacity at constant pressure, B^S is the adiabatic bulk modulus, and T is the absolute temperature.

4. Results

Transit time measurements were made which resulted in values of

$$C' = (C_{11} - C_{12})/2\,,\ C_{11}^S\,, \text{ and } C_n^S = C_{11}^S - C' + C_{44}\,.$$

The values of C_{44}, B^S, and B^T were calculated from the three measured constants using the well-known relations

$$C_{44} = C_n^S - C_{11}^S + C'\,, \tag{5}$$

$$B^S = C_{11}^S - \tfrac{4}{3}\,C'\,, \tag{6}$$

and

$$B^T = \frac{B^S}{1 + \Delta}.$$

Table 1 presents the results of the analysis of the data for C_{11}^S, and C_n^S and C' evaluated at 100 °K, as well as the constants C_{44}, and B^S and B^T which have been computed from the measured values.

Two other sets of atmospheric pressure ultrasonic data are available [18, 19]. These and the present absolute values evaluated at 100 °K are itemized in Table 2.

Table 3 compares the results of three calculations (Fuchs [24], Boffey [25], and Suzuki et al. [30]) with the three sets of absolute value data extrapolated to $T = 0$ °K. In the case of the Nash and Smith data, where only three temperature points were taken, the extrapolation is somewhat more uncertain than for either of the other two sets.

Table 4 contains a summary of temperature derivatives. The present data agrees most often with that published by Slotwinsik and Trivisonno [19]. This would reasonably be the case as the number of points used to determine the slope in that data is large compared to the number of points for the Nash and Smith data.

Swenson [41], on the basis of direct PVT measurements, obtained a value of $\mathrm{d}B^T/\mathrm{d}T = -5 \times 10^{-2}$ kbar/deg contrasted to the present value of -6×10^{-2} kbar/deg.

The zero temperature extrapolated pressure derivatives are compared with those derived theoretically by Suzuki et al. [30], in Table 5. The Suzuki data was calculated using a core radius value of 1.36 at. units. Using a value of 0.92 at. units the agreement between the calculated and experimental pressure derivatives is much better but the values of the calculated elastic constants are changed greatly by this choice of core radius.

Table 6 compares the pressure derivatives of the shear constants C' and C_{44} given by Jain [27] with the present results. The agreement is very good.

The values of B_0^T and $(\mathrm{d}B_0^T/\mathrm{d}P)_T$ obtained by various methods are summarized in Table 6.

The shock values are obtained from Rice's [42] measured values of c and s in the rela-

Table 1

Results of curve fitting temperature and pressure data

	C_{11}^S	C_n^S	C'	C_{44}	B^S	B^T
C (kbar) $T = 100$ °K $P = 0$ kbar	142.3 ± 0.7	238.0 ± 0.9	11.3 ± 0.02	107.0 ± 0.9	127.2 ± 0.7	126.5 ± 0.7
$\mathrm{d}C/\mathrm{d}T$ (10^{-2} kbar deg^{-1}) $P = 0$ kbar	−4.75 ± 0.2	−14.1 ± 0.4	−0.42 ± 0.02	−9.8 ± 0.5	−4.2 ± 0.2	−6.0 ± 0.2
$\mathrm{d}C/\mathrm{d}P$ (dimensionless) $T = 100$ °K	3.44 ± 0.1	4.36 ± 0.2	0.06 ± 0.01	0.98 ± 0.2	3.36 ± 0.1	3.38 ± 0.1
$\mathrm{d}^2C/\mathrm{d}T\,\mathrm{d}P$ (deg^{-1})	0.08 ± 0.09	0.12 ± 0.17	0.01 ± 0.005	0.05 ± 0.26	0.07 ± 0.10	0.09 ± 0.10

Table 2

Values of elastic constants from various sources.
Units of kbar, $T = 100$ °K, $P = 0$ kbar

C_{11}^S	C_n^S	C'	C_{44}	B^S	reference
146.0	240.3	11.5	105.8	130.7	[18]
143.5	239.4	11.0	107.3	128.8	[19]
142.3	238.0	11.3	107.0	127.2	present paper

Table 3

Experimental and theoretical values of elastic constants *) from various sources.
Units of 10^2 kbar, $T = 0$ °K, $P = 0$ kbar

	C_{11}	C_n	C'	C_{44}	B	reference
(calc)	1.53	2.69	0.17	1.33	1.30	[24]
(calc)	1.50	2.54	0.12	1.16	1.34	[30]
(calc)			0.11	1.11		[25]
(exp)	1.54	2.55	0.119	1.13	1.38	[18]
(exp)	1.47	2.49	0.112	1.13	1.32	[19]
(exp)	1.46	2.48	0.116	1.14	1.31	present paper

*) Adiabatic and isothermal elastic constants and bulk moduli are equal at $T = 0$ °K.

Table 4

Temperature derivatives of elastic constants from various sources evaluated at 300 °K.
Units of 10^{-2} kbar deg^{-1}, $P = 0$ kbar

$\mathrm{d}C_{11}^S/\mathrm{d}T$	$\mathrm{d}C_n^S/\mathrm{d}T$	$\mathrm{d}C'/\mathrm{d}T$	$\mathrm{d}C_{44}/\mathrm{d}T$	$\mathrm{d}B^S/\mathrm{d}T$	reference
-11.8	-21.5	-0.6	-10.3	-11.0	[18]
-4.7	-13.7	-0.3	-9.3	-4.3 *)	[19]
-4.75	-14.1	-0.42	-9.8	-4.2	present paper

*) Value tabulated in Table 2 of [19] is -3.1 but this appears to be in error.

tion $u_s = c + s u_p$, where

$$c = \left(\frac{B_0^S}{\varrho_0}\right)^{1/2} \quad \text{and} \quad s = \frac{1}{4}\left[\left(\frac{\mathrm{d}B_0^S}{\mathrm{d}P}\right)_S + 1\right], \tag{7}$$

and u_s and u_p are the shock and particle velocities, respectively. The adiabatic quantities are then converted to isothermal quantities. The results for both B_0^T and $(\mathrm{d}B_0^T/\mathrm{d}P)$ at 300 °K are good (Table 7).

5. Discussion

One motivating force of the present work was the desire to test the validity of 1. the bulk elastic instability concept proposed by Zener for b.c.c. metals, and 2. a microscopic elastic instability argument, as possible mechanisms for martensitic-type transformations. None of the three sets of data indicate a bulk elastic instability. All room pressure elastic constants have negative temperature

Table 5

Experimental pressure derivatives extrapolated to zero temperature compared to calculated pressure derivatives, dimensionless

	$\mathrm{d}C_{44}/\mathrm{d}P$	$\mathrm{d}C'/\mathrm{d}P$	$\mathrm{d}B/\mathrm{d}P$	core radius	reference
(calc)	1.7	0.25	3.5	1.36	[30]
(calc)	1.0	0.09	3.2	0.92	[30]
(exp)	0.93	0.05	3.3		present paper

Table 6

Pressure derivatives of the shear elastic constants C_{44} and C' from Jain [27] and present work; dimensionless, $T = 300$ °K

$\mathrm{d}C_{44}/\mathrm{d}P$	$\mathrm{d}C'/\mathrm{d}P$	reference
1.03	0.081	[27]
1.08	0.08	present paper

Table 7

Values of B_0^T and $(\mathrm{d}B_0^T/\mathrm{d}P)_T$ at 300 °K

B_0^T (kbar)	$(\mathrm{d}B_0^T/\mathrm{d}P)_T$	method
110	—	ultrasonic [18]
116	—	ultrasonic [19]
115	3.56 ± 0.1	ultrasonic (present)
112	3.60 ± 0.3	volumetric [41]
109	3.5	shock [42]

coefficients to the lowest temperatures measured. What is more, at any pressure within the range of the present experiments, the temperature coefficients of all of the elastic constants remain negative.

The present data also indicates that the microscopic instability concept does not apply to the martensitic transformation in lithium. The data shows that at all temperature–pressure points within the region (85 to 300 °K, 1 bar to 3.5 kbar) all of the elastic constants have negative temperature and positive pressure derivatives. It is conceivable that although $\mathrm{d}C'/\mathrm{d}P$ is positive at 3.5 kbar it becomes negative at higher pressure, so that C' does in fact become negative at a finite pressure such as one that might be present in a dislocation core. It is possible that the microscopic instability is not evident at low pressures. If C' were to go to zero at 22 kbar as the microscopic instability theory suggests, then $\mathrm{d}C'/\mathrm{d}P$ at 3.5 kbar should already be -0.14 kbar. At temperatures within 20 °K of the transformation, the quantity $\mathrm{d}C'/\mathrm{d}P$ could not be continuously monitored, thus a small negative change, if it did exist, could well be masked by the absolute value measurement errors. Detection then would require accurate measurement of the second derivative, $\mathrm{d}^2C'/\mathrm{d}P^2$, to considerably higher pressures than the 3.5 kbar of the present experiments. Even under the best of conditions the measurement of $\mathrm{d}^2C'/\mathrm{d}P^2$ is a difficult task.

6. Conclusions

1. The present results, evaluated at $T = 300$ °K and atmospheric pressure, are not in sharp disagreement with previous elastic constant data published by Nash and Smith [18] and Slotwinski and Trivisonno [19].

2. The present elastic constant temperature derivatives fall between those of Nash and Smith and of Slotwinski and Trivisonno.

3. The pressure derivatives of C_{44} and C' are in excellent agreement with those published by Jain [27] at 300 °K.

4. When account is taken of the non-sphericity of the Fermi surface of lithium, the calculated zero-temperature elastic constants are in error by only a few percent when compared to the three sets of extrapolated experimental values.

5. The present data on lithium indicate that the elastic constants above the martensitic transformation temperature do not show evidence of the impending transformation. There is as yet no evidence that either the bulk elastic instability concept proposed by Zener or the microscopic elastic instability put forward here apply to the martensitic transformation in lithium.

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