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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 dC'/dT at pressure, to determine the applicability of the bulk elastic instability hypothesis originally postulated by Zener [7, 8], and dC'/dP 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) [110] 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

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.