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PREDICTION OF HIGH PRESSURE PHASE TRANSITIONS BY ELASTIC CONSTANT DATA

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Abstract

The Born elastic stability criterion provides a useful method of predicting polymorphic transitions at high pressure. Elastic constants can be extrapolated to high pressure, and a phase transition must occur before any of the shear elastic constants vanish. Many pressure-induced transitions are related to a macroscopic shear of the crystal lattice, in which cases, the dimensionless ratio of the shear elastic constant to the bulk modulus C_t/K is related to the curvature of the free energy along the reaction coordinate leading from the low-pressure to the high-pressure phase, and this ratio is a crude indicator of the Gibbs free energy difference between the two phases.

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We calculate the free energy for a model lattice as it transforms continuously from the NaCl to the CsCl lattice at a number of pressures to demonstrate this connection between the shear elastic constant C_{44} and the pressure-induced phase change. We have measured the single crystal elastic constants of KCl from zero pressure to the phase transition at 20 kbar. These data show that the elastic constants vary linearly with pressure right up to the transition, when the shear constant C_{44} has decreased to the relatively low value of only 20.6% of the bulk modulus. In other alkali halides, we infer similar behavior of the ratio $\alpha = C_{44}/K$ at the transition from the extrapolation of low-pressure elastic constant data, and find similar behavior for other pressure-induced phase transitions with α usually in the range 0.15-0.20. This modification of the Born criterion can be used to predict phase transitions in several compounds when C_{44}/K decreases to a critical value.

I. INTRODUCTION

The experimental study of the polymorphism of solids under pressure is an important tool for learning more about solids and the earth's interior. A good theory to predict phase relations under pressure will be useful in helping to choose experiments that are most likely to yield useful results. Predictions could be applied to minerals or other solids of interest, which are either inaccessible to current experiments or for which results are not yet available.

A comprehensive theory based on a direct calculation of free energy differences is not available. The idea of using the extrapolation of data on the elastic constants at low pressures to predict transitions at high pressure by means of the Born criterion has been around for quite a while. In many cases, the Born criterion was used to predict a transition at the pressure at which a shear elastic constant reached zero; however, experimental evidence now shows that the transition takes place before this pressure.

In Section II of this paper, we show that the transition should take place when the shear constant reaches a critical fraction, α, of the bulk modulus. This new modification of the Born criterion makes possible improved predictions of the transition pressure in cases for which a shear elastic constant decreases under pressure, and also it permits good predictions when a shear constant increases very slowly with pressure.

In Section III, we present new experimental data on the elastic properties of KCl up to the phase transition at 20 kbar. This data is in excellent agreement with our theory.

In Section IV of this article, we gather together an assortment of data on elastic constants and phase transitions to try to test how well the modified Born criterion works, and we make some