

Divergences Among the Born and Classical Stability Criteria for Cubic Crystals under Hydrostatic Loading

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The classical criterion for the stability of cubic crystals under constant hydrostatic pressure is distinguished from the notional criterion of stability introduced by Born. Although the latter has been widely used in the literature, theoretical computations demonstrate appreciable quantitative and qualitative divergences between the criteria. The computations are made within the framework of a crystal model that is both mathematically tractable and sufficiently realistic for the intended purpose.

The classical Lagrange-Dirichlet criterion for elastic stability, when applied to a cubic crystal under a hydrostatic pressure P that does not vary during any departure from a considered configuration of equilibrium, gives

$$\kappa(P) > 0, \quad \mu(P) > 0, \quad \mu'(P) > 0, \quad (1)$$

as shown briefly by Hill and Milstein.¹ Here κ is the bulk modulus, while μ and μ' are the usual shear moduli in the relation between the cubic-axes components of the Cauchy stress increment $\delta\sigma_{ij}$ and the rotationless strain increment $\delta\epsilon_{ij}$ (reckoned relative to the *current* configuration under P). A fully rigorous derivation of (1) via the modern theory of bifurcation for elastic continua is presented by Milstein and Hill²; the treatment is classical in that (i) the loading environment is fully specified, to sufficient order and in both its active and passive modes, and (ii) the potential energy of the system as a whole is examined in all the nearby, possibly inhomogeneous, configurations allowed by the kinematic constraints, if any.

The classical approach is distinguished from the notion of crystal stability instituted by Born and variously implemented by later writers. In what is popularly known as the "Born stability criterion," positive definiteness of the current matrix of elastic moduli, $C_{rs} = \partial^2 W / \partial q_r \partial q_s$, is taken to be synonymous with stability. Here W is the energy per atom (or, equivalently, per unit cell) and q_r , $r = 1, \dots, 6$, are generalized coordinates, namely geometric variables that define the homogeneous strain of the crystal; various choices of the q_r can be found in the literature. Although not mentioned by Born, consistency of

this notion with the classical criterion, in the sense of (i) and (ii) above, requires a special environment in which the loads can be varied so as to "follow" the material during any disturbances and keep fixed the values of the conjugate forces, $\partial W / \partial q_r$, for the particular choice of generalized coordinates; these forces may consequently become different in kind from those in the configuration of equilibrium whose stability is under test. For cubic crystals under hydrostatic loading, the Born criterion leads to

$$C_{11} + 2C_{12} > 0, \quad C_{11} - C_{12} > 0, \quad C_{44} > 0. \quad (2)$$

At zero load (1) and (2) are naturally equivalent, but when $P \neq 0$, they predict different domains of stability; moreover, the conditions (2) are thoroughly "relative" in the sense that they are dependent on the choice of generalized coordinates, since the convexity of W is not coordinate invariant under load.³ In practice the Born school automatically took q_r , $r = 1, \dots, 6$, to be Cartesian components of the Green measure of strain relative to the unloaded state, and there was no attempt to match the analysis to a practicable physical situation⁴⁻⁶; the same can be said of all other choices in the literature. The relevant passages from Born's papers are quoted in Ref. 7.

We have completed a detailed numerical investigation of the domains of classical stability for the entire family of Morse-function cubic crystals (fcc, bcc, and sc) under hydrostatic loading, and have studied the possible bifurcations at the domain limits. Particular attention was given to the roles of lattice structure and effective range of the interatomic potential. For comparison we have also examined the domains of Born stability

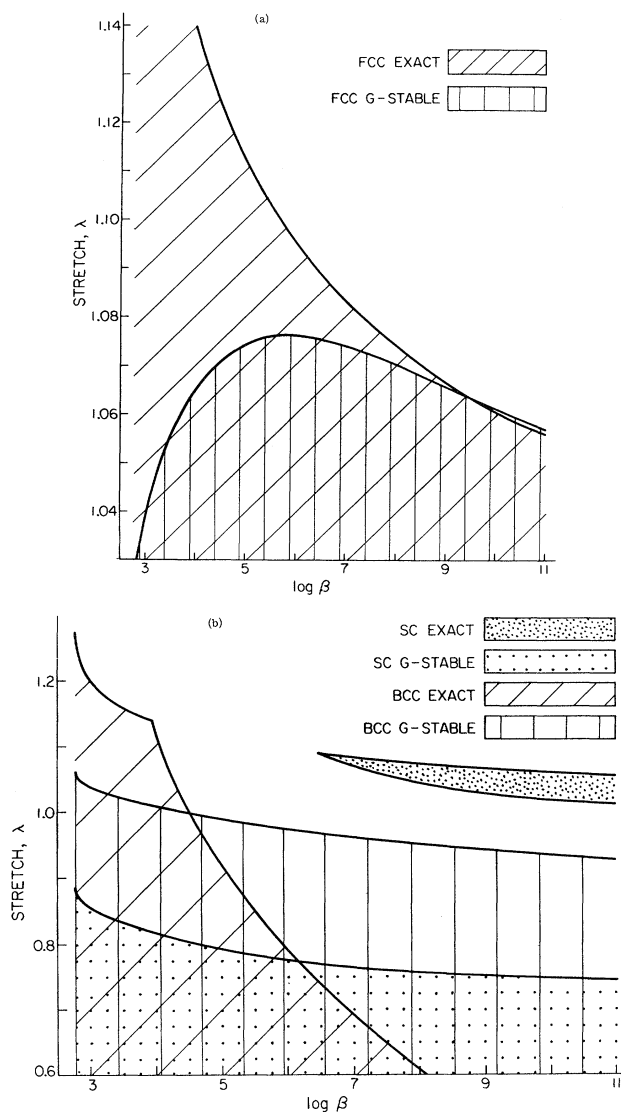


FIG. 1. Ranges of classical stability in a hydrostatic environment, and of convexity of the strain energy relative to the Green variables, for the Morse family of monatomic cubic crystals: (a) fcc, (b) bcc and sc. The lattices are classically stable according to (2) with the Green variables in the regions indicated as "G-STABLE."

for several choices of the generalized coordinates. It is found that the ranges of Born stability are quite sensitive to the choice of coordinates, and that significant qualitative and quantitative differences occur between the ranges of Born and classical stability.

For the three cubic lattices, Fig. 1 shows the domains of classical stability, indicated as "exact," and of Born stability when the coordinates are in particular the components of Green's strain, indicated as "G stable." Any two atoms

at a current separation R in the crystal are assumed to interact according to a Morse function $\varphi(R) = D \{ \exp[-2\alpha(R - r_0)] - 2 \exp[-\alpha(R - r_0)] \}$, and W is determined by summing over a sufficiently large number of interactions to obtain convergence (see Refs. 8–10 for the computation procedure). The parameter $\beta \equiv \exp(\alpha r_0)$ can be interpreted as an effective-potential-range indicator: Thus, larger $\ln \beta$ means shorter range and steeper functions $\varphi(R)$ (see Fig. 2 of Ref. 9). The current volume per atom is $\lambda^3 V$, where V is the volume per atom when $P = 0$ and λ is the all-around stretch. Realistic values of $\ln \beta$, calculated from experimental data, vary from about 3 to 8.^{11,12} For each lattice the range of classical (as well as Born) stability depends uniquely on the value of $\ln \beta$.^{2,9,10}

Marked quantitative differences are found in the ranges of classical and Born stability for each of the three lattices. Qualitative divergences are also present; for example, for the fcc structure, the range of classical stability decreases monotonically as $\ln \beta$ increases, whereas the G-stable range increases with $\ln \beta$ below about 6. Also, the "exact" range of stability of the sc lattice exists only in volumetric expansion, while the Born G-stable range is in compression. We note, in passing, that this work is apparently the first where a theoretical range of stability has been revealed for sc crystals.

An extensive account of this work is to be presented in a full journal article elsewhere.²

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²F. Milstein and R. Hill, to be published.

³R. Hill, Math. Proc. Cambridge Philos. Soc. **77**, 225 (1975).

⁴M. Born, Proc. Cambridge Philos. Soc. **36**, 160 (1940).

⁵M. Born and R. Fürth, Proc. Cambridge Philos. Soc. **36**, 454 (1940).

⁶R. Fürth, Proc. Cambridge Philos. Soc. **37**, 177 (1941).

⁷Born discussed his basic idea of lattice stability in Ref. 4, where he wrote

"If $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are the vectors describing the cell we have to take as the molar parameters the six scalar products $\vec{a}_r \cdot \vec{a}_s = a_{rs}$ ($r, s = 1, 2, 3$)... The generalized forces corresponding to the molar parameters a_{rs} are the stress components

$$A_{rs} = -(\partial A / \partial a_{rs}) \quad (1.5)$$

which are determined by the external conditions (for instance, for a hydrostatic pressure $A_{11}=A_{22}=A_{33}=p$, $A_{23}=A_{31}=A_{12}=0$). By solving these equations we find the equilibrium values of the a_{rs} (for instance, for a cubic cell $a_{11}=a_{22}=a_{33}=a^2$, $a_{23}=a_{31}=a_{12}=0$). Not every solution is stable, but only those for which the quadratic terms in the expansion of A , with respect to small alterations δa_{rs} of the a_{rs} from their equilibrium values a_{rs}^0 , are positive definite. These terms have the form

$$A - A_0 = \frac{1}{2} \sum_{\rho\sigma} A_{rs, \rho\sigma}(T) \delta a_{rs} \delta a_{\rho\sigma},$$

$$A_{rs, \rho\sigma} = \left(\frac{\partial^2 A}{\partial a_{rs} \partial a_{\rho\sigma}} \right)_0 \quad (1.6)$$

... If we now go to the limit of vanishing temperature, the free energy A becomes identical with the static potential energy U . But the stability conditions remain valid even in this limiting case where the thermodynamic system degenerates into a mechanical one. We must infer that the macroscopic stability of the lattice is determined by the positive definite character of the quadratic form (1.6) (where A is now replaced by U) of six variables only, the variations δa_{rs} of the cell parameters, ...

Born concluded Ref. 4 by stating "... the calculation of the strength of crystals should be attacked by the

method developed in this paper. This work will be carried out by my collaborators and pupils." In Ref. 5, Born and Fürth directly applied the Born stability criterion, as quoted above, to a crystal subjected to a particular mode of loading, viz. (100) uniaxial. In Ref. 6, Fürth (as communicated by Born) employed the same criterion in a discussion of the stability of cubic crystals under hydrostatic pressure, viz. "The stability condition for a cubic lattice under uniform stress in the direction of one of the axes (Born and Fürth, 1940) can easily be transformed into the stability conditions for a uniform pressure p in all directions. We have only to assume that the atomic distances are equal for all three axes, that is, the constant c introduced in (Born and Fürth, 1940) is equal to b , and ... replace the equilibrium conditions (12) of that paper by the conditions $F_i^0(b, b, b) = p/2a^2$ ($i = 1, 2, 3$) where a is the lattice constant for zero pressure."

⁸F. Milstein, Phys. Rev. B **3**, 1130 (1971), and **10**, 3635 (1974), and **18**, 2529 (1978).

⁹F. Milstein and R. Hill, J. Mech. Phys. Solids **25**, 457 (1977).

¹⁰F. Milstein and R. Hill, J. Mech. Phys. Solids **26**, 213 (1978).

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¹²F. Milstein, Phys. Rev. B **2**, 512 (1970).

Spectroscopy of Phonon Scattering in Glass

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This Letter investigates the phonon scattering in SiO₂ glass at frequencies above 100 GHz by phonon spectroscopy with superconducting tunnel junctions. By analyzing the frequencies of the scattered phonons with two independent techniques, evidence is obtained for strong inelastic phonon scattering in glass. Furthermore, the phonon mean free path is determined as a function of the phonon frequency.

The thermal conductivity (κ) of practically all glassy materials shows a number of common features which are quite different from those of crystalline materials.^{1,2} Below about 1 K, κ is proportional to the temperature squared. This was explained³ by the scattering of the phonons by two-level systems⁴ which were studied extensively by ultrasonic techniques.⁵ Above 1 K, the thermal conductivity is nearly temperature independent forming the so-called "plateau".¹⁻³ The phonon scattering processes, however, which lead to the plateau are at present not understood.

Several theories were proposed. Zeller and Pohl suggested a strong Rayleigh-like scattering which decreases the phonon mean free path l with

ω^{-4} (ω being the phonon frequency).¹ Zaitlin and Anderson extended the theory of the low-temperature regime to higher temperatures by assuming a density of states of the two-level systems with a term quadratic in energy.⁶ Leadbetter *et al.* proposed that the phonons undergo Raman scattering at the two-level systems.⁷ They expected this process to increase with the fourth power of frequency. All three theories provided good fits to the thermal conductivity data, so that no distinction was possible so far. Further, the resulting fit parameters were questioned for all three cases by Jones, Thomas, and Phillips.⁸ Therefore, more specific information is needed. This can be provided by phonon spectroscopy