Existence of a negative Poisson ratio in fcc crystals

Frederick Milstein and K. Huang
University of California, Santa Barbara, California 93106
(Received 5 August 1977)

The Poisson ratios along two principal crystal directions normal to a [110] uniaxial load are generally of opposite algebraic sign for fcc crystals. A theoretical basis for this behavior is revealed.

The initial Poisson's ratios

$$\nu_{1\bar{1}0} \equiv -\epsilon_{1\bar{1}0}/\epsilon_{110} \text{ and } \nu_{001} \equiv -\epsilon_{001}/\epsilon_{110}, \quad (1)$$

along two natural principal axes of a cubic crystal subjected to uniaxial [110] loading can be related to the elastic moduli C^0_{ij} of the unloaded crystal by the expressions

$$\nu_{1\bar{1}0} = (R - 2C^0_{44})/(R + 2C^0_{44}),$$

and

$$\nu_{001} = 4C^0_{12}C^0_{44}/C^0_{11}(R + 2C^0_{44}), \quad (2)$$

where

$$R \equiv C^0_{11} + C^0_{12}(1 - 2C^0_{12}/C^0_{11}).$$

Table I shows a compilation of experimental values of elastic moduli of fcc metals and rare-gas

TABLE I. Elastic constants C^0_{ij} (in 10^{12} dyn/cm^2) and Poisson's ratios $\nu_{1\bar{1}0}$ and ν_{001} (as calculated from the C^0_{ij}) for fcc crystals.

Crystal	Temperature (°K)	Reference	C^0_{11}	C^0_{12}	C^0_{44}	$\nu_{1\bar{1}0}$	ν_{001}
Pd	0	1	2.341	1.761	0.712	0.010	0.745
	50		2.336	1.768	0.707	0.005	0.753
	100		2.319	1.768	0.701	−0.004	0.765
	150		2.291	1.753	0.702	−0.015	0.777
	200		2.270	1.743	0.706	−0.028	0.789
	250		2.262	1.744	0.711	−0.038	0.801
	300		2.271	1.761	0.717	−0.049	0.813
Th	0	1	0.778	0.482	0.513	−0.215	0.753
	300		0.753	0.489	0.478	−0.223	0.794
Cu	0	2	1.762	1.249	0.818	−0.138	0.806
	300		1.684	1.214	0.754	−0.136	0.819
Ag	0	2	1.315	0.973	0.511	−0.093	0.809
	300		1.240	0.937	0.461	−0.096	0.828
Au	0	2	2.016	1.697	0.454	−0.029	0.867
	300		1.923	1.631	0.420	−0.032	0.876
Al	0	2	1.143	0.619	0.316	0.267	0.397
	300		1.068	0.607	0.282	0.272	0.414
Pb	0	2	0.555	0.454	0.194	−0.186	0.970
	300		0.495	0.423	0.149	−0.209	1.033
Ni	0	2	2.612	1.508	1.317	−0.051	0.607
	300		2.508	1.500	1.235	−0.055	0.631
Ne	4.7	3	0.0169	0.0097	0.0100	−0.13	0.65
	24.3	4	0.0118	0.0074	0.0060	−0.095	0.69
Ar	4	5	0.0411	0.0190	0.0210	0.006	0.459
	4.2	6	0.0367	0.0174	0.0234	−0.11	0.526
	82.3	7	0.0238	0.0156	0.0112	−0.083	0.710
Kr	0	8	0.0506	0.0287	0.0273	−0.078	0.611
Xe	151	9	0.0303	0.0190	0.0156	−0.10	0.69

solids. The moduli were used in Eqs. (2) to calculate the Poisson's ratios $\nu_{1\bar{1}0}$ and ν_{001}, which also are given in Table I. In almost all cases, $\nu_{1\bar{1}0}$ is negative. (The only notable exception in the table is Al; the positive values at low temperatures for Pd and Ar are probably smaller in magnitude than the experimental error.) The values of ν_{001} are all positive. The implication is that, in general, when a uniaxial load is applied along a [110] direction (a face diagonal) of a fcc crystal, the strain $\epsilon_{1\bar{1}0}$ (i.e., along the perpendicular face diagonal) will be of the *same* algebraic sign as the strain ϵ_{110} in the direction of loading and of opposite algebraic sign to the strain ϵ_{001} along the other principal normal (i.e., the [001] cube edge).

It is the intention of this paper to present insight into the basis for the behavior described above. An incidental objective is also to point up the utility of studying relatively simple theoretical crystal models *at large strains* as a means of obtaining deeper understanding of the bases for elastic properties of real crystals in their *reference* or *unstrained* equilibrium states. For these purposes, we first consider "constructing" a fcc crystal according to the following "thought experiment."

Start with a bcc crystal in its unloaded equilibrium (but not necessarily stable) state; the lengths of the edges of the bc cell are b_1, b_2, and b_3. Consider a primary path of deformation to be defined by the condition that the crystal be loaded uniaxially in the b_1 direction only; that is, the only force is one acting normal to the 2-3 face of the bc unit cell. Along this path, emanating from the bcc state, $b_2 = b_3 \neq b_1$, in general. As recently shown by Hill and Milstein,[10] at the point at which $C_{22} = C_{23}$ (along such a path) there is a special "coordinate invariant" bifurcation. The bifurcation is coordinate invariant in the sense that it occurs at the same point on the primary path, irrespective of the choice of geometric coordinates q_r used in specifying the strain (assuming a "reasonable" choice with regard to lattice symmetry); the strain variables are used in the definition of the elastic moduli, viz., $C_{rs} = \partial^2 w / \partial q_r \partial q_s$; w is the internal energy per unit cell of the crystal. We can presume that the "$C_{22} = C_{23}$" state exists, in general (with a possible exception being a case in which the values of C_{22} and C_{23} remain parallel or diverge in *both* compression and elongation). The nature of the bifurcation associated with this state is as follows: all loads remain stationary (no loads act on the 1-2 or 1-3 faces of the bc cell and the uniaxial load remains *dead*[11]); the b_i remain orthogonal; b_1 remains stationary ($\delta b_1 = 0$); and b_2 and b_3 vary according to $\delta b_2 = -\delta b_3$ (the δ symbol indicates an incremental change). With no loss of generality, we can assume the following: first,

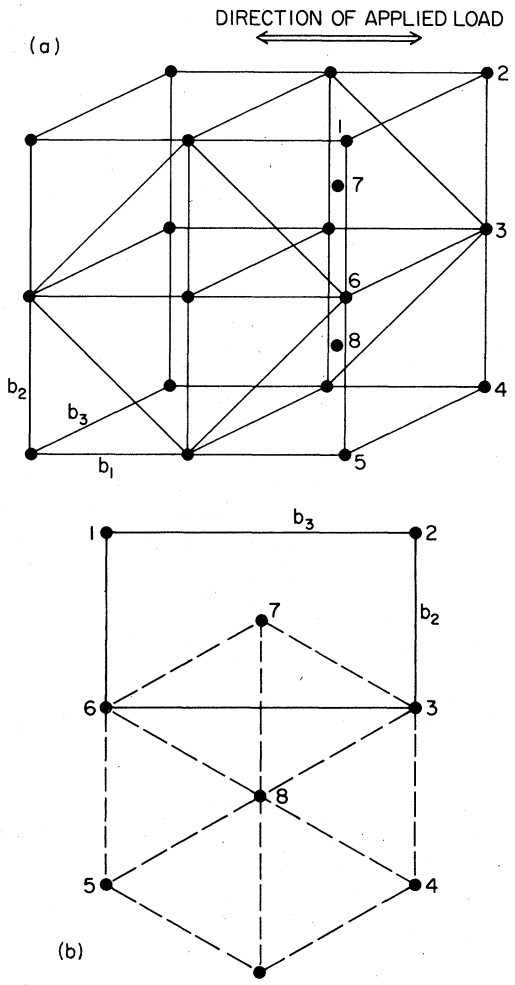

FIG. 1. (a) Portion of the lattice showing four body-centered (bc) cells and a face-centered (fc) cell contained within the bc cells. Lattice sites 7 and 8 are in the "centers" of two of the bc cells shown and on the faces of the fc cell. (b) "Side view" (i.e., view normal to the planes containing b_2 and b_3) of portion of lattice shown in Fig. 1(a), illustrating the "close-packed" relationship at very high [110] uniaxial compression.

the bcc crystal is considered to be loaded uniaxially (as described) to the state $C_{22} = C_{23}$; second, at this state, the crystal undergoes the indicated bifurcation (i.e., $\delta b_1 = 0$, $\delta b_3 = -\delta b_2$); and third, the crystal then follows a *new branch* of the primary equilibrium path, along which the loading continues to remain uniaxial and normal to the 2-3 plane, and the b_i remain orthogonal and vary in a manner that $b_1 \neq b_2 \neq b_3$, in general.

In order to be more definite about the "$b_2 \neq b_3$" branch, it is necessary to rely on specific theoretical calculations. However, the following working hypotheses are not unreasonable: (i) With reference to Fig. 1(a), a face centered cell is readily

located within four adjacent body-centered cells. Let us presume that this fc cell passes through the fcc configuration at some state of the equilibrium "$b_2 \neq b_3$" branch. (ii) Since the bifurcation leading from the "$b_2 = b_3$" branch to the "$b_2 \neq b_3$" branch is of such nature that the initial slopes $\delta b_2/\delta b_1$ and $\delta b_3/\delta b_1$ are of opposite algebraic sign and of *infinite* magnitude, let us presume that $\delta b_2/\delta b_1$ and $\delta b_3/\delta b_1$ remain of opposite algebraic sign over a large range of the "$b_2 \neq b_3$" branch, and let this range include the fcc state.

If hypothesis (i) is true, it follows, from considerations of crystal symmetry and the nature of the loading path, that the fcc state is stress free (since the 1-2 plane is stress free) and furthermore that the branch of the equilibrium path under consideration is identical to the primary loading path of unconstrained [110] uniaxial loading of the fcc crystal. If, in addition, hypothesis (ii) is true, it follows that the initial Poisson's ratios, indexed relative to the fcc unit cell, are such that $\nu_{1\bar{1}0}$ and ν_{001} are of opposite algebraic sign, in agreement with experimental values for a wide selection of fcc crystals. If, finally, in addition, we make the hypothesis (iii) that the "$b_2 \neq b_3$" path proceeds in the direction of decreasing b_1 (after branching from the "$b_2 = b_3$" path at state $C_{22} = C_{23}$), it then follows that it is the Poisson's ratio $\nu_{1\bar{1}0}$ that is negative.

Detailed theoretical calculations have verified hypothesis (i)–(iii) for a particular crystal model (in which the strain energy comes solely from pairwise interactions between atoms). The elastic moduli were calculated,[12] relative to the bc cell, according to $C_{ij} = \partial^2 w/\partial b_i \partial b_j$; the conditions of equilibrium were specified such that the uniaxial force $F_1 = \partial w/\partial b_1$ and the remaining forces $F_i = \partial w/\partial b_i \equiv 0$, $i = 2, 3$. In the present paper we relate the Poisson's ratios to the C_{ij}, and examine the theoretical path dependencies of these ratios along the "$b_2 \neq b_3$" branch.

The quantitative details of the theoretical behavior discussed in the remainder of this paper apply to (i.e., " have been verified for") the particular crystal model studied in Ref. 12. However, in view of the generality of the conditions $\nu_{1\bar{1}0} < 0$ and $\nu_{001} > 0$ for fcc crystals, we believe that the qualitative theoretical behavior has fairly general applicability.

The *incremental* Poisson's ratios *at any stage* can be written as

$$\nu_{1\bar{1}0} \equiv -\frac{b_1}{b_2}\frac{\delta b_2}{\delta b_1} \quad \text{and} \quad \nu_{001} \equiv -\frac{b_1}{b_3}\frac{\delta b_3}{\delta b_1}. \tag{3}$$

In the unloaded fcc state, Eqs. (3) coincide with Eqs. (1). Also, at any stage, an incremental variation along the path satisfies $\delta F_i \simeq C_{ij}\delta b_j \equiv 0$ for $i = 2$ and 3 (summation convention, $j = 1, 2, 3$), from which

$$\delta b_2/\delta b_1 \simeq (C_{13}C_{23} - C_{12}C_{33})/D, \tag{4}$$

and

$$\delta b_3/\delta b_1 \simeq (C_{12}C_{23} - C_{13}C_{22})/D, \tag{5}$$

where $D = C_{22}C_{33} - C_{23}^2$. The right-hand sides of Eqs. (4) and (5) are, of course, db_2/db_1 and db_3/db_1, respectively; the values of C_{ij} calculated in Ref. 12 are used here in Eqs. (4) and (5) to evaluate db_2/db_1 and db_3/db_1 along the path corresponding to [110] uniaxial loading. The results are shown in Figs. 2(a) and 2(b). The stretches λ_i are defined

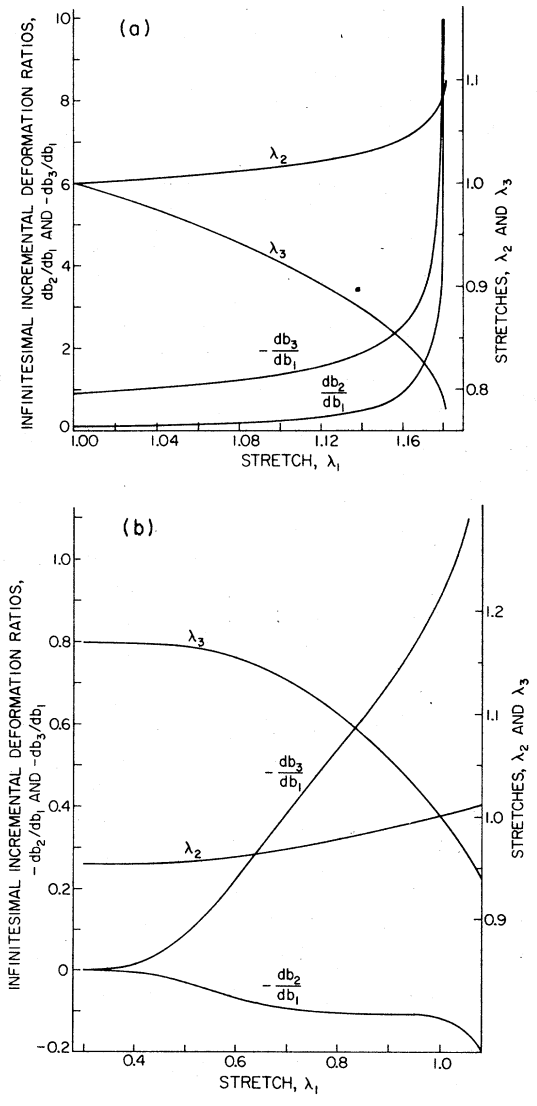

FIG. 2. Principal stretches λ_2 and λ_3 (normal to the loading direction) and infinitesimal incremental deformation ratios vs stretch λ_1 (in the loading direction) for the [110] uniaxial loading of a fcc crystal. (a) Region of elongation; (b) primarily region of compression.

as follows: if the lattice parameters of the bc cell are b_i in the current state and b_i^0 in the unloaded fcc state ($b_1^0 = b_2^0 = b_3^0/\sqrt{2}$), then $\lambda_i = b_i/b_i^0$. (Although the λ_i are defined at any state of loading, in the particular immediate neighborhood of the fcc state, $\lambda_1 \simeq 1 + \epsilon_{110}$, $\lambda_2 \simeq 1 + \epsilon_{1\bar{1}0}$, and $\lambda_3 \simeq 1 + \epsilon_{001}$.) Figure 2(a) shows the region of elongation. As λ_1 increases, λ_2 also increases, while λ_3 decreases. As the state corresponding to the invariant bifurcation (connecting the "$b_2 \neq b_3$" branch with the "$b_2 = b_3$" branch) is approached along the "$b_2 \neq b_3$" branch [shown in Fig. 2(a)], the following behavior is found: $C_{22} \to C_{23}$; $b_2 \to b_3$ and hence $C_{22} \to C_{33}$ and $C_{12} \to C_{13}$ (this state occurs at about $\lambda_1 = 1.18$). The denominator D and both of the numerators of the right-hand sides of Eqs. (4) and (5) approach zero; however, D approaches zero more rapidly, and $db_2/db_1 \to \infty$ and $db_3/db_1 \to -\infty$.

In the region of high uniaxial compression, as λ_1 decreases, $C_{12} \to 0$ and $C_{13} \to 0$; thus from Eqs. (3)–(5), $\nu_{1\bar{1}0} \to 0$ and $\nu_{001} \to 0$ (λ_2 and λ_3 approach constant values); this behavior is seen in Fig. 2(b). As λ_1 became small, successive parallel crystallographic planes normal to the direction of loading became arranged in a "close packed" manner. This arrangement is illustrated in Fig. 1(b). As λ_1 increases along the path of [110] uniaxial loading, the ratio b_3/b_2 varies monotonically from $\sqrt{3}$ (at very small λ_1), through $\sqrt{2}$ (at $\lambda_i = 1$, $i = 1, 2, 3$), to 1 (at the invariant "$C_{22} = C_{23}$" state). The limiting geometric behavior of the lattice under high uniaxial compression is therefore also very revealing of the bases for the elastic behavior in the neighborhood of the stress-free fcc state.

Finally, we might mention a possibly interesting connection between the results of the present studies and experimental investigations of martensitic transformations. Gunton and Saunders[13] have associated the martensitic transformation (in indium and indium thallium alloys), from a fcc phase to a tetragonal phase, with a negative instability of the Poisson's ratio $\nu_{1\bar{1}0}$; i.e., $\nu_{1\bar{1}0}$ is negative in algebraic sign and as the transformation is approached, the magnitude of this negative quantity increases. In the present study, a *stress-free* tetragonal state was found along the equilibrium [110] uniaxial loading path at $\lambda_1 \simeq 1.170$ (fairly close to the invariant $C_{22} = C_{23}$ state). However, in the present crystal model, the stress-free tetragonal crystal structure was mechanically unstable.

ACKNOWLEDGMENTS

The research of one of us (F.M.) was supported in part by a John Simon Guggenheim Memorial Fellowship and in part by a NATO Senior Fellowship administered by the NATO Senior Scientists Program. Parts of this work were completed while F. M. was on leave at Department of Applied Mathematics and Theoretical Physics, University of Cambridge, England, and a Visiting Fellow at Clare Hall.

[1]R. F. S. Hearmon, *Landolt-Bornstein, Group III* (Springer, Berlin, 1966), Vol. I.
[2]C. Kittel, *Introduction to Solid State Physics*, 4th ed. (Wiley, New York, 1971).
[3]S. Gewurtz, H. Kiefte, D. Landheer, R. A. McLaren, and B. P. Stoicheff, Phys. Rev. Lett. 29, 1454, 1768(E) (1972).
[4]J. A. Leake, W. B. Daniels, J. Skalyo, B. C. Frazer, and G. Shirane, Phys. Rev. 181, 1251 (1969).
[5]D N. Batchelder, M. F. Collins, B. C. G. Haywood, and G. R. Sidey, J. Phys. C 3, 249 (1970).
[6]H. Egger, M. Gsänger, E. Lüscher, and B. Dorner, Phys. Lett. A 28, 433 (1968); B. Dorner and H. Egger, Phys. Status Solidi B 43, 611 (1971).
[7]S Gewurtz and B. P. Stoicheff, Phys. Rev. B 10, 3487 (1974).
[8]J. A. Barker, M. V. Bobetic, and M. L. Klein, Phys. Lett. A 34, 415 (1971).
[9]W. S. Gornall and B. P. Stoicheff, Phys. Rev. B 4, 4518 (1971).
[10]R. Hill and F. Milstein, Phys. Rev. B 15, 3087 (1977).
[11]R. Hill, Math. Proc. Camb. Philos. Soc. 77, 225 (1975).
[12]F. Milstein and K. Huang, Phys. Rev. B 18, 2529 (1978).
[13]D J. Gunton and G. A. Saunders, Proc. R. Soc. A 343, 63 (1975).