Generalized set of elastic moduli and stability of deformed cubic crystals

K. P. Thakur and Shafique Ahmad
Department of Physics, Tej Narayan Banaili College, Bhagalpur University, Bhagalpur 812 007, India
(Received 21 April 1986; revised manuscript received 19 August 1986)

A generalized set of strain variables, q_r^N, has been used to develop the expressions for a generalized set of elastic moduli, C_{rs}^N, for a cubic crystal deformed to the orthorhombic structure. The coordinates q_r^N and elastic moduli C_{rs}^N are shown to be the generalization of the corresponding quantities derived from the strain variables currently used for theoretical strength studies. Numerical results for the theoretical stability of nickel on the path of deformation connecting the unstressed fcc and bcc phases of the crystal have been presented according to the generalized set of strain variables using the Morse potential and the stability criterion of Born. Values of the lattice parameters at which failure occurs (for N stability) are determined and cases under which the N strength (crystal strength in terms of the generalized variables) becomes greater or smaller than the other conventional strengths are discussed.

I. INTRODUCTION

Elastic properties of solids have been extensively studied[1-8] because a large amount of information concerning mechanical behavior and other elastic-constant-dependent properties of deformed solids can be gathered from these studies. In particular, the theory of elasticity forms the basis for the estimation of the theoretical strength of any loaded structure with the elastic moduli as the central core in theories of mechanical stability of solids under stress. In these theories, there are six fundamental deformations and the specification of the state of homogeneous strain in a crystal model involves any six variables that define the geometry of the most fundamental cell. In practice, different researchers have adopted different sets of generalized coordinates q_r ($r=1,2,\ldots,6$) as the measure of homogeneous strain to develop various sets of elastic moduli leading to the computation of the ideal strength of crystals under stress.

In this paper, a generalized set of strain variables q_r^N that we have defined earlier[9] is used to develop the expressions for a generalized set of elastic moduli C_{rs}^N for cubic crystal deformed to orthorhombic structure. The set of geometric variables q_r^N are shown to be the generalization of the other conventional sets of strain variables, namely, the Green's variables adopted by Born and coworkers[10-14] and the stretch variables adopted by Macmillan and Kelly.[15-17] The elastic moduli corresponding to the stretch variables and Green's variables are shown to be particular members of the generalized set C_{rs}^N. Finally, the theoretical stability of nickel on the path of deformation connecting the stress-free fcc and stress-free bcc phases of the crystal is estimated according to the generalized set of strain variables. Computations are made of the lattice parameters, internal energies, stresses, and elastic moduli using the two-body Morse potential function. The numerical values of N moduli C_{rs}^N thus computed along the prescribed path of deformation, are then used to determine the range of N stability (crystal strength in terms of q_r^N) according to the stability criterion of Born.[10] In specific cases the N strength so estimated is shown to be greater (or smaller) than the crystal strengths generated by the stretch variables and Green's variables.

These studies are very important in several phenomena of solid-state physics and solid mechanics. The problem of evaluating the stability limits of a crystal is of fundamental interest since it is thought that some fine filaments and metallic whiskers can approach the theoretical limit. The problem is also relevant in the prediction of the stress distribution near the tip of a crack and hence, in determining whether a solid will exhibit brittle or ductile behavior.[18-20] Moreover, twinning, very rapid shock deformation, martensitic phase transition, and deformation of whiskers are also problems which involve the ideal strength of solid.

II. THEORETICAL APPROACH

A. Strain variables and associated moduli

In order to study the strength of deformed solids and their elastic properties we need a set of geometric variables which define the strains of the deformed solid. For this purpose, Born and co-workers have used the components of Green's tensor,[10-14] whereas the recent papers of Macmillan and Kelly[15-17] incorporate the components of the stretch tensor. However, we have recently defined a generalized set of geometric variables,[9] under the summation convention

$$q_{ij}^N=\frac{1}{2m}[(m-n)\lambda_{ki}\lambda_{kj}+2n\lambda_{ij}-(m+n)\delta_{ij}]\ , \qquad (1)$$

where δ_{ij} is the Kronecker delta; n and m can assume any suitable values, positive or negative, with the restriction that $m\neq 0$, and λ_{ij} are the elements of the stretch tensor defined by

$$x_i=\sum_j \lambda_{ij}X_j,\quad \lambda_{ij}=\lambda_{ji}\ , \qquad (2)$$

($i,j=1,2,3$) where X_i and x_i are, respectively, the refer-

ence and current rectangular coordinates of any lattice vector.

The coordinates corresponding to the generalized set of strain variables [Eq. (1)] may explicitly be expressed by

$$q_1^N=\frac{1}{2m}[(m-n)(\lambda_1^2+\lambda_5^2+\lambda_6^2)+2n\lambda_1-(m+n)];\ldots;\ldots,$$
$$q_4^N=\frac{1}{m}\{(m-n)[(\lambda_2+\lambda_3)\lambda_4+\lambda_5\lambda_6]+2n\lambda_4\};\ldots;\ldots, \tag{3}$$

where the tensor notation (ij) is converted to the matrix notation (r) according to the scheme $(11)\rightarrow 1$, $(22)\rightarrow 2$, $(33)\rightarrow 3$, $(23)\rightarrow 4$, $(31)\rightarrow 5$, $(12)\rightarrow 6$. It is interesting to note that for $n=0$, Eq. (3) reduces to

$$2q_1^G=\lambda_1^2+\lambda_5^2+\lambda_6^2-1;\ldots;\ldots,$$
$$q_4^G=(\lambda_2+\lambda_3)\lambda_4+\lambda_5\lambda_6;\ldots;\ldots, \tag{4}$$

which represent the coordinates q_r^G corresponding to the Green's strain tensor adopted by Born school.[10-14] Also, after taking $n=m$, Eq. (3) reduces to

$$q_1^S=\lambda_1-1;\ldots;\ldots,$$
$$q_4^S=2\lambda_4;\ldots;\ldots, \tag{5}$$

representing the coordinates corresponding to the stretch variables used by Macmillan and Kelly.[15-17] Thus the present form of the generalized set of strain variables q_r^N [Eq. (3)] is capable of reproducing Green's variables q_r^G and the stretch variables q_r^S in special cases. Moreover, relation (3) can lead to any desired set of strain variables depending upon the choices of the parameters m and n.

The generalized forces[10] corresponding to the set of strain variables q_r^N are the stress components

$$F_{ij}=\frac{\partial E}{\partial q_{ij}^N}, \tag{6}$$

which are determined by the external loading conditions. The internal energy E per unit reference cell may be expressed as a function of the geometric variables $q_r(r=1,2,\ldots,6)$

$$E=E(q_1,q_2,\ldots,q_6).$$

For computational purposes, the internal energy E can be taken as a pairwise sum of interactions $\phi(r)$ over a large number of atoms in the lattice to obtain convergence up to significant figures

$$E=\frac{N}{2}\sum_{l_1}\sum_{l_2}\sum_{l_3}\phi(r), \tag{7}$$

and

$$r^2=\tfrac{1}{4}(l_1^2a_1^2+l_2^2a_2^2+l_3^2a_3^2). \tag{8}$$

a_i $(i=1,2,3)$ represents the vectors coincident with the cell edges, whereas its magnitude $|a_i|$ represents the cell length. The stretch $\lambda_i=a_i/a_0$; a_0 being the cell length of the unstressed reference cell. N is the number of atoms per unit cell (four for fcc lattice and two for bcc lattice). Summations in above equations are to be accomplished over integral values of l_1,l_2,l_3 subject to the restrictions that $l_1+l_2+l_3$ is even for the reference cell to be fcc; l_1,l_2,l_3 are all odd or all even when the bcc cell is chosen as the reference.

The elastic moduli C_{rs} can be defined by

$$C_{rs}=\frac{\partial^2 E}{\partial q_r\partial q_s}, \tag{9}$$

where q_r $(r=1,2,\ldots,6)$ are generalized coordinates, namely, geometric variables that define the homogeneous strain of the crystal. In particular, when the generalized coordinates q_r are the components of the set of strain variables q_r^N, one may use relations (3) in conjunction with the definition (9) to obtain expressions for the set of generalized moduli C_{rs}^N. For cubic crystals, as the unstressed reference state which under load deforms to the orthorhombic structure we obtain, for the generalized set of elastic moduli expressed in terms of the interatomic potential function $\phi(r)$,

$$C_{iiii}^N=\frac{m^2\lambda_i^2}{[(m-n)\lambda_i+n]^2}\frac{Na_0}{8}\sum_{l_1}\sum_{l_2}\sum_{l_3}l_i^4\frac{\partial^2\phi(r)}{\partial(r^2)^2}+\frac{m^2n}{[(m-n)\lambda_i+n]^3}\frac{N}{4}\sum_{l_1}\sum_{l_2}\sum_{l_3}l_i^2\frac{\partial\phi(r)}{\partial r^2},\quad (i=1,2,3),$$
$$C_{iijj}^N=\frac{m^2\lambda_i\lambda_j}{[(m-n)\lambda_i+n][(m-n)\lambda_j+n]}\frac{Na_0}{8}\sum_{l_1}\sum_{l_2}\sum_{l_3}l_i^2l_j^2\frac{\partial^2\phi(r)}{\partial(r^2)^2},\quad (i,j=1,2,3;\ i\neq j), \tag{10}$$
$$C_{ijij}^N=\frac{m^2}{[(m-n)(\lambda_i+\lambda_j)+2n]^2}\left[(\lambda_i+\lambda_j)^2\frac{Na_0}{8}\sum_{l_1}\sum_{l_2}\sum_{l_3}l_il_jl_il_j\frac{\partial^2\phi(r)}{\partial(r^2)^2}+\frac{n}{(m-n)\lambda_i+n}\frac{N}{4}\sum_{l_1}\sum_{l_2}\sum_{l_3}l_i^2\frac{\partial\phi(r)}{\partial r^2}\right.$$
$$\left.+\frac{n}{(m-n)\lambda_j+n}\frac{N}{4}\sum_{l_1}\sum_{l_2}\sum_{l_3}l_j^2\frac{\partial\phi(r)}{\partial r^2}\right],\quad (i,j=1,2,3;\ i\neq j).$$

The derivation of Eqs. (10) is given in the Appendix.

It is wise to note here that for $n=0$ in Eq. (10), the set of generalized moduli C_{rs}^N reduces to the set of Green's moduli C_{rs}^G used by Born and co-workers:[10-14]

$$C_{rs}^{G}=C_{ijkl}^{G}=\frac{Na_0}{8}\sum_{l_1}\sum_{l_2}\sum_{l_3}l_i l_j l_k l_l\frac{\partial^2\phi(r)}{\partial(r^2)^2}\ , \tag{11}$$

and after taking $n=m$ in relations (10) we find that the C_{rs}^{N} reduces to the stretch moduli C_{rs}^{S}, a choice of Macmillan and Kelly:[15–17]

$$C_{iiii}^{S}=\lambda_i^2\frac{Na_0}{8}\sum_{l_1}\sum_{l_2}\sum_{l_3}l_i^4\frac{\partial^2\phi(r)}{\partial(r^2)^2}+\frac{N}{4}\sum_{l_1}\sum_{l_2}\sum_{l_3}l_i^2\frac{\partial\phi(r)}{\partial r^2},\quad (i=1,2,3)$$

$$C_{iijj}^{S}=\lambda_i\lambda_j\frac{Na_0}{8}\sum_{l_1}\sum_{l_2}\sum_{l_3}l_i^2 l_j^2\frac{\partial^2\phi(r)}{\partial(r^2)^2},\quad (i,j=1,2,3;\ i\neq j) \tag{12}$$

$$C_{ijij}^{S}=\tfrac{1}{4}\left[(\lambda_i+\lambda_j)^2\frac{Na_0}{8}\sum_{l_1}\sum_{l_2}\sum_{l_3}l_i l_j l_i l_j\frac{\partial^2\phi(r)}{\partial(r^2)^2}+\frac{N}{4}\sum_{l_1}\sum_{l_2}\sum_{l_3}(l_i^2+l_j^2)\frac{\partial\phi(r)}{\partial r^2}\right],\quad (i,j=1,2,3;\ i\neq j)\ .$$

Thus we see that in special cases the C_{rs}^{N} can lead to the Green's moduli C_{rs}^{G} and the stretch moduli C_{rs}^{S}. Moreover, the set of generalized moduli C_{rs}^{N} is capable of reproducing any desired set of elastic moduli depending upon the choices of m and n.

B. Stability of fcc nickel on the path of fcc→bcc transformation

As a specific example of the present approach, a theoretical study is made of the lattice stability or theoretical strength of fcc nickel subjected to the path of deformation connecting the stress-free fcc and stress-free bcc phases of the crystal. Computations of lattice parameters, stresses, internal energies, and a few members of the general family of elastic moduli C_{rs}^{N} are performed. Calculations are carried out using the two-body Morse potential model:

$$\phi(r)=D\{\exp[-2\alpha(r-r_0)]-2\exp[-\alpha(r-r_0)]\}\ , \tag{13}$$

where $\phi(r)$ is the potential energy between two atoms separated by a distance r, D is the dissociation energy, and α, r_0 are the potential parameters.

With the selection of the unstressed fcc cell as the reference state which under load deforms to orthorhombic structure, the three normal components of the generalized forces, specifying the state of loading for the crystal, is given by

$$F_i=\frac{ma_0}{(m-n)\lambda_i+n}\frac{\partial E}{\partial a_i}\ . \tag{14}$$

The stress σ_i acting along a_i direction is then[21]

$$\sigma_i=\frac{F_i}{a_j a_k}\ . \tag{15}$$

We have for the fcc phase of the crystal

$$a_1=a_2=a_3\ . \tag{16}$$

Whereas for the bcc phase[21,22]

$$\sqrt{2}a_1=a_2=a_3\ . \tag{17}$$

The line joining the stress-free bcc and stress-free fcc phases may be represented by[23]

$$a_2=A_0+A_1 a_1 \tag{18}$$

where A_0 and A_1 are constants given by

$$A_0=a_0\frac{a_1-a_2}{a_1-a_0}$$

and

$$A_1=\frac{a_2-a_0}{a_1-a_0}\ .$$

C. Criteria of stability

The Born stability criterion[10] may be expressed as the convexity of the internal energy function E in its arguments or, synonymously, the positive definiteness of the matrix of elastic moduli C_{rs} [Eq. (9)], regardless of the choice of generalized coordinates q_r $(r=1,2,\ldots,6)$ defining the homogeneous strain of the crystal. For cubic crystals under multidirectional stresses the Born stability criterion leads to

$$\begin{aligned}&C_{22}-C_{23}>0\ ,\\ &C_{22}+C_{23}-2(C_{12})^2/C_{11}>0\ ,\\ &C_{44}>0\ ,\\ &C_{55}>0\ .\end{aligned} \tag{19}$$

It is important to note that in a crystal under load, the conditions (19) are thoroughly relative in the sense that they are dependent upon the choice of the generalized coordinates[21,22] and generate different domains of lattice stability for various choices of q_r. However, the only one generated by an appropriate set of coordinates can be right.

III. RESULTS AND DISCUSSION

The C_{rs}^{N}, calculated (with $\lambda_2=\lambda_3$, for the present case of loading) from Eq. (10) using the Morse function (13) with $\alpha=2.487\,655$ Å^{-1}, $r_0=2.527\,516$ Å, $D=0.35059\times10^{-12}$ erg and $a_0=3.5238$ Å taken from the compilation of

our earlier paper,[22] are used to determine the range of N stability according to the criteria (19).

The values of cell lengths a_1, a_2 $(=a_3)$ are calculated on the line noted in Eqs. (16) and (17), for which the stresses $\sigma_i=0$ $(i=1,2,3)$ by calculating zeroes of functions. The cell length $b_0=2.81$ Å thus obtained corresponds to the stress-free bcc phase of nickel. Computed values of internal energy E are plotted against cell length a_1 in Fig. 1. The plot exhibits two internal energy minima; the principal minimum corresponds to the equilibrium fcc state of the crystal whereas the secondary minimum arises near the predicted bcc phase. The energy barrier for the fcc→bcc transition in nickel is of the order of 0.44×10^{-12} erg per unit fcc cell.

We have calculated only few members of the general family of elastic moduli, C_{rs}^N, with a limited choice of m and n (for $m=2$, and $n=-2,-1,0,1,\ldots,20$). The quantities $C_a^N=C_{22}^N-C_{23}^N$ and $C_b^N=C_{22}^N+C_{23}^N-2(C_{12}^N)^2/C_{11}^N$ appearing in the stability conditions (19) are examined for their positive definiteness and the values of lattice parameters at the onset of lattice instability (for N stability) are calculated. For different choices of m and n, instability occurs almost in the same region ($a_1=2.71$ to 3.23 Å with the corresponding values of $a_2=4.05$ to 3.71 Å), where the condition $C_b^N>0$ is violated. But the condition $C_a^N>0$ is violated at different cell lengths for different choice of m and n. Figure 2, showing the variation of cell length a_1, at which the criterion $C_a^N>0$ is violated, as a function of n, keeping $m=2$, exhibits that the cell length a_1 decreases with increasing n. This indicates that the width of the stable region (for N stabilities) decreases with increase in n, keeping $m=2$.

For $m=2$, $n=0$, the range of N stability becomes equal to the range of G stability (3.23 Å $\le a_1 \le$ 3.93 Å) while at $m=n=2$, it becomes equal to the range of S stability (3.23 Å $\le a_1 \le$ 3.84 Å). At $m=2$, $n=1$ (i.e., both m and n positive with $n<m$) the N strength will evidently comes in between the G and S strengths [Fig. (2)]. For both m and n positive with $n>m$ (i.e., for $m=2$, $n=3,4,\ldots,20$), Fig. 2 indicates that N stability breaks at cell lengths smaller than the values of cell lengths corresponding to the G and S instability implying thereby that the N strength is less than the S strength, which in turn is less than G strength. Under the same loading environment for $m=2$, $n=-1$, one can predict from Fig. 2 that the N-stable range is greater than the G-stable and S-stable ranges (i.e., the N strength is greater than G strength, which in turn is greater than the S strength). Thus we see that, in specific cases (i.e., depending upon the values of m and n) the generalized set of strain variables can generate crystal strength somewhat different (smaller or greater) from the strength obtainable from the Green's variables and the stretch variables.

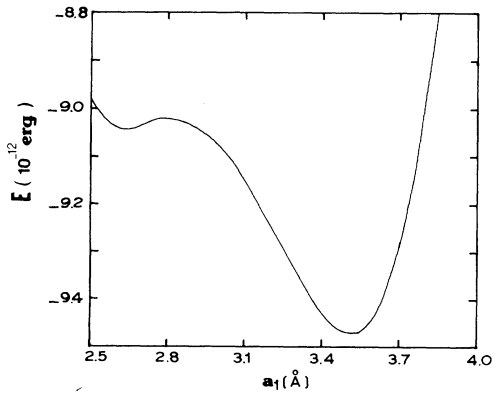

FIG. 1. Internal energy $E(10^{-12}$ erg) per unit cell of nickel versus cell length a_1.

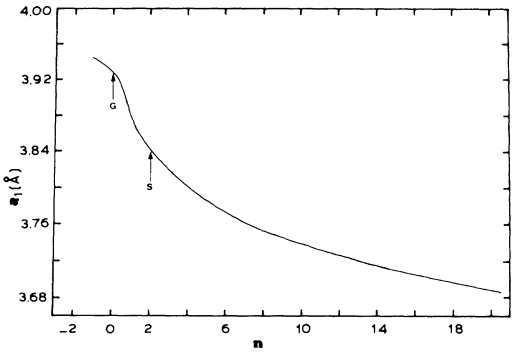

FIG. 2. Variation of cell length a_1 (Å) at which the criterion $C_a^N=C_{22}^N-C_{23}^N>0$ is violated for nickel, as a function of the parameter n, keeping $m=2$. Failure points corresponding to the G stability and S stability are shown to occur, respectively, at $n=0$ and at $n=m=2$.

IV. SUMMARY AND CONCLUSION

A generalized set of strain variables q_r^N has been used to frame expressions for a generalized set of elastic moduli C_{rs}^N for cubic crystals deformed under load to orthorhombic structures. It is interesting to note that the generalized coordinates q_r^N and the set of generalized moduli C_{rs}^N reduce, respectively, to Green's coordinate q_r^G and Green's moduli C_{rs}^G, after taking $n=0$ in Eqs. (3) and (10). Also, after taking $n=m$ in these equations, the q_r^N and C_{rs}^N reduce, respectively, to the stretch coordinates q_r^S and the stretch moduli C_{rs}^S. Thus the coordinates q_r^N and elastic moduli C_{rs}^N are the generalization of the corresponding terms derived from the Green's and stretch variables. Also, the q_r^N represents a family of the generalized coordinates of which the Green's coordinates, $q_r^G(q_r^N$ with $n=0)$ and the stretch coordinates $q_r^S(q_r^N$ with $n=m)$ are the particular members. Similarly, the C_{rs}^N also represent a family of elastic moduli, the Green's moduli C_{rs}^G and the stretch moduli C_{rs}^S are the members of this family of elastic moduli.

Further, the paper presents the computational results on the stability of nickel crystal on the line of deformation connecting the stress-free bcc and stress-free fcc phases, in terms of the generalized variables. The results, as summarized in Fig. 2, indicate that in special cases the range of N stability becomes equal to the range of G stability and the range of S stability. The range of lattice de-

formation (for N stability) varies with varying choices of n and m. Moreover, from these studies one would expect the presence of the stress-free bcc phase of nickel with a cell length of 2.81 Å and energy $E=-9.023\times10^{-12}$ erg per unit cell corresponding to the stress-free bcc phase of the crystal. The detailed nature of the fcc→bcc phase transformation in a number of metals including fcc nickel has been studied and reported[23] separately.

In principle one can have many more choices of the geometric variables to define the homogeneous strain of crystals under stress. We have chosen the present generalized form since (i) it is the generalization of the two widely used geometric variables, viz., the Green's variable and stretch variable, (ii) it has the property to generate not only the Green's moduli and stretch moduli but also various other sets of elastic moduli of deformed solids, and (iii) this variable can yield crystal strength, smaller or greater than the G strength and S strength depending upon the choices of m and n. In the stress-free state the assessment of elastic stability of cubic crystals is coordinate invariant. The Born criteria for stability apply to any coordinates for the geometric variables, and hence yield different stability ranges depending upon the choice of geometric variables. However, only one can be right, and only one set of coordinates appropriate. Uncertainties in these studies also arise from the choice of the potential model. Thus one has to evolve some specific criteria for selecting a particular geometric variables in conjunction with a realistic potential model on the basis of observed properties of the loaded crystal (which are very much lacking today) to have a better understanding of the mechanical behavior of the deformed crystals.

ACKNOWLEDGMENTS

The authors thank the University Grants Commission (New Delhi) and Council of Scientific and Industrial Research (New Delhi) for financial assistance.

APPENDIX

Expressions for C_{rs}^N [Eq. (10)] can be derived using Eqs. (3), (4), (8), and (9). For example, a detailed derivation of the moduli C_{11}^N, C_{12}^N, and C_{44}^N is given here. By the definition (9) we have

$$C_{11}^N=\frac{\partial^2 E}{\partial q_1^N\partial q_1^N}=\frac{\partial}{\partial q_1^N}\left[\frac{\partial E}{\partial q_1^N}\right]=\frac{\partial}{\partial q_1^N}\left[\frac{\partial E}{\partial r^2}\frac{\partial r^2}{\partial q_1^N}\right]. \tag{A1}$$

From Eqs. (3) and (8) we have, respectively,

$$\frac{\partial\lambda_1}{\partial q_1^N}=\frac{m}{(m-n)\lambda_1+n}, \tag{A2}$$

and

$$\frac{\partial r^2}{\partial a_1}=\tfrac{1}{2}a_1 l_1^2 .$$

Now

$$\frac{\partial r^2}{\partial q_1^N}=\frac{\partial r^2}{\partial a_1}\frac{\partial a_1}{\partial\lambda_1}\frac{\partial\lambda_1}{\partial q_1^N}=\tfrac{1}{2}a_0^2 l_1^2\frac{m\lambda_1}{(m-n)\lambda_1+n}, \tag{A3}$$

where $\lambda_1=a_1/a_0$.

Substituting for $\partial r^2/\partial q_1^N$, Eq. (A1) gives

$$C_{11}^N=\frac{\partial}{\partial q_1^N}\left[\tfrac{1}{2}a_0^2 l_1^2\frac{m\lambda_1}{(m-n)\lambda_1+n}\frac{\partial E}{\partial r^2}\right]$$

$$=\tfrac{1}{2}a_0^2 l_1^2 m\left\{\left[\left[\left[(m-n)\lambda_1+n\right]\frac{\partial\lambda_1}{\partial q_1^N}-\lambda_1(m-n)\frac{\partial\lambda_1}{\partial q_1^N}\right]\Big/\left[(m-n)\lambda_1+n\right]^2\right]\frac{\partial E}{\partial r^2}+\frac{\lambda_1}{(m-n)\lambda_1+n}\frac{\partial^2 E}{\partial(r^2)^2}\frac{\partial r^2}{\partial q_1^N}\right\}$$

which on using Eqs. (A2) and (A3) in conjunction with Eq. (7) gives for C_{11}^N the expression

$$C_{11}^N=\frac{m^2\lambda_1^2}{[(m-n)\lambda_1+n]^2}\frac{Na_0}{8}\sum_{l_1}\sum_{l_2}\sum_{l_3}l_1^4\frac{\partial^2\phi(r)}{\partial(r^2)^2}+\frac{m^2 n}{[(m-n)\lambda_1+n]^3}\frac{N}{4}\sum_{l_1}\sum_{l_2}\sum_{l_3}l_1^2\frac{\partial\phi(r)}{\partial r^2}, \tag{A4}$$

For C_{12}^N we have from (9)

$$C_{12}^N=\frac{\partial^2 E}{\partial q_1^N\partial q_2^N}=\frac{\partial}{\partial q_1^N}\left[\frac{\partial E}{\partial q_2^N}\right]=\frac{\partial}{\partial q_1^N}\left[\frac{\partial E}{\partial r^2}\frac{\partial r^2}{\partial q_2^N}\right]=\frac{\partial}{\partial q_1^N}\left[\tfrac{1}{2}a_0^2 l_2^2\frac{m\lambda_2}{(m-n)\lambda_2+n}\frac{\partial E}{\partial r^2}\right], \tag{A5}$$

where

$$\frac{\partial r^2}{\partial q_2^N}=\tfrac{1}{2}a_0^2 l_2^2\frac{m\lambda_2}{(m-n)\lambda_2+n},$$

and

$$\lambda_2=\frac{a_2}{a_0}. \tag{A6}$$

Carrying out the differentiation in (A5) we have

$$C_{12}^N=\tfrac{1}{2}a_0^2l_2^2m\left\{\frac{\lambda_2}{(m-n)\lambda_2+n}\frac{\partial^2E}{\partial(r^2)^2}\frac{\partial r^2}{\partial q_1^N}+\left[\left[(m-n)\lambda_2+n\right]\frac{\partial\lambda_2}{\partial q_1^N}-\lambda_2(m-n)\frac{\partial\lambda_2}{\partial q_1^N}\right]\Big/\left[(m-n)\lambda_2+n\right]^2\right]\frac{\partial E}{\partial r^2}\right\}.$$

Substituting for $\partial r^2/\partial q_1^N$ from Eq. (A3) we have, since $\partial\lambda_2/\partial q_1^N=0$,

$$C_{12}^N=\frac{m^2\lambda_1\lambda_2}{[(m-n)\lambda_1+n][(m-n)\lambda_2+n]}\frac{a_0^4}{4}l_1^2l_2^2\frac{\partial^2E}{\partial(r^2)^2},$$

which on using Eq. (7), gives

$$C_{12}^N=\frac{m^2\lambda_1\lambda_2}{[(m-n)\lambda_1+n][(m-n)\lambda_2+n]}\times\frac{Na_0}{8}\sum_{l_1}\sum_{l_2}\sum_{l_3}l_1^2l_2^2\frac{\partial^2\phi(r)}{\partial(r^2)^2}. \tag{A7}$$

Next, for C_{44}^N we have from (9)

$$C_{44}^N=\frac{\partial^2E}{\partial q_4^N\partial q_4^N}=\frac{\partial}{\partial q_4^N}\left[\frac{\partial E}{\partial q_4^N}\right]=\frac{\partial}{\partial q_4^N}\left[\frac{\partial E}{\partial\lambda_4}\frac{\partial\lambda_4}{\partial q_4^N}\right]. \tag{A8}$$

From Eq. (3), we have

$$\frac{\partial\lambda_4}{\partial q_4^N}=\frac{m}{(m-n)(\lambda_2+\lambda_3)+2n}. \tag{A9}$$

Equations (A8) and (A9) together lead to

$$C_{44}^N=\frac{\partial}{\partial q_4^N}\left[\frac{m}{(m-n)(\lambda_2+\lambda_3)+2n}\frac{\partial E}{\partial\lambda_4}\right]$$
$$=\frac{m}{(m-n)(\lambda_2+\lambda_3)+2n}\frac{\partial^2E}{\partial\lambda_4^2}\frac{\partial\lambda_4}{\partial q_4^N}-\left[m(m-n)\left[\frac{\partial\lambda_2}{\partial q_4^N}+\frac{\partial\lambda_3}{\partial q_4^N}\right]\Big/\left[(m-n)(\lambda_2+\lambda_3)+2n\right]^2\right]\frac{\partial E}{\partial\lambda_4}.$$

Again from Eq. (3), we get

$$\frac{\partial\lambda_2}{\partial q_4^N}=\frac{\partial\lambda_3}{\partial q_4^N}=\frac{m}{(m-n)\lambda_4}. \tag{A10}$$

Using Eqs. (A9) and (A10) we obtain for C_{44}^N, the expression

$$C_{44}^N=\frac{m^2}{[(m-n)(\lambda_2+\lambda_3)+2n]^2}\left[\frac{\partial^2E}{\partial\lambda_4^2}-\frac{2}{\lambda_4}\frac{\partial E}{\partial\lambda_4}\right]$$
$$=\frac{m^2}{[(m-n)(\lambda_2+\lambda_3)+2n]^2}\left[\frac{\partial^2E}{\partial\lambda_4^2}-\frac{1}{\lambda_4}\left[\frac{\partial E}{\partial q_2^N}\frac{\partial q_2^N}{\partial\lambda_4}+\frac{\partial E}{\partial q_3^N}\frac{\partial q_3^N}{\partial\lambda_4}\right]\right]$$
$$=\frac{m^2}{[(m-n)(\lambda_2+\lambda_3)+2n]^2}\left[\frac{\partial^2E}{\partial\lambda_4^2}-\frac{m-n}{m}\left[\frac{\partial E}{\partial q_2^N}+\frac{\partial E}{\partial q_3^N}\right]\right], \tag{A11}$$

making substitution from Eq. (A10). Now using relations like (A3) and (A6), we have

$$\frac{\partial E}{\partial q_2^N}=\frac{\partial E}{\partial r^2}\frac{\partial r^2}{\partial q_2^N}=\tfrac{1}{2}a_0^2l_2^2\frac{m\lambda_2}{(m-n)\lambda_2+n}\frac{\partial E}{\partial r^2},$$
$$\frac{\partial E}{\partial q_3^N}=\frac{\partial E}{\partial r^2}\frac{\partial r^2}{\partial q_3^N}=\tfrac{1}{2}a_0^2l_3^2\frac{m\lambda_3}{(m-n)\lambda_3+n}\frac{\partial E}{\partial r^2}. \tag{A12}$$

Equations (A11) and (A12) together lead to

$$C_{44}^N=\frac{m^2}{[(m-n)(\lambda_2+\lambda_3)+2n]^2}\times\left[\frac{\partial^2E}{\partial\lambda_4^2}-[(m-n)/2]\left[\frac{\lambda_2}{(m-n)\lambda_2+n}a_0^2l_2^2\frac{\partial E}{\partial r^2}+\frac{\lambda_3}{(m-n)\lambda_3+n}a_0^2l_3^2\frac{\partial E}{\partial r^2}\right]\right]. \tag{A13}$$

From the relation

$$r^2=\frac{a_0^2}{2}(l_1^2q_1^G+l_1^2+l_2^2q_2^G+l_2^2+l_3^2q_3^G+l_3^2+l_2l_3q_4^G+l_1l_3q_5^G+l_1l_2q_6^G), \tag{A14}$$

for the triclinic deformation, we have

$$\frac{\partial r^2}{\partial q_2^G}=\frac{a_0^2}{2}l_2^2,\quad\frac{\partial r^2}{\partial q_3^G}=\frac{a_0^2}{2}l_3^2,$$

and

$$\frac{\partial r^2}{\partial q_4^G}=\frac{a_0^2}{2}l_2l_3. \tag{A15}$$

Also the relations (4) give

$$\frac{\partial q_4^G}{\partial\lambda_4}=\lambda_2+\lambda_3,\quad\frac{\partial q_2^G}{\partial\lambda_2}=\lambda_2, \tag{A16}$$

and

$$\frac{\partial q_2^G}{\partial \lambda_4}=\frac{\partial q_3^G}{\partial \lambda_4}=\lambda_4 .$$

Now

$$\frac{\partial^2 E}{\partial \lambda_4^2}=\frac{\partial}{\partial \lambda_4}\left[\frac{\partial E}{\partial q_4^G}\frac{\partial q_4^G}{\partial \lambda_4}\right]=\frac{\partial}{\partial \lambda_4}\left[(\lambda_2+\lambda_3)\frac{\partial E}{\partial q_4^G}\right] .$$

Differentiating partially and then making substitutions from Eqs. (A15) and (A16), the above equation reduces to

$$\frac{\partial^2 E}{\partial \lambda_4^2}=(\lambda_2+\lambda_3)^2\frac{a_0^4}{4}l_2^2 l_3^2\frac{\partial^2 E}{\partial (r^2)^2}+\frac{a_0^2}{2}l_2^2\frac{\partial E}{\partial r^2}+\frac{a_0^2}{2}l_3^2\frac{\partial E}{\partial r^2} . \tag{A17}$$

Substituting for $\partial^2 E/\partial \lambda_4^2$ in Eq. (A13) and then using Eq. (7) we get for C_{44}^N the expression

$$C_{44}^N=\frac{m^2}{[(m-n)(\lambda_2+\lambda_3)+2n]^2}\left[(\lambda_2+\lambda_3)^2\frac{Na_0}{8}\sum_{l_1}\sum_{l_2}\sum_{l_3}l_2^2 l_3^2\frac{\partial^2\phi(r)}{\partial (r^2)^2}+\frac{n}{(m-n)\lambda_2+n}\frac{N}{4}\sum_{l_1}\sum_{l_2}\sum_{l_3}l_2^2\frac{\partial\phi(r)}{\partial r^2}\right.$$

$$\left.+\frac{n}{(m-n)\lambda_3+n}\frac{N}{4}\sum_{l_1}\sum_{l_2}\sum_{l_3}l_3^2\frac{\partial\phi(r)}{\partial r^2}\right] . \tag{A18}$$

[1]F. J. Rizzo and D. J. Shippy, J. Elast. **13**, 91 (1983).
[2]R. C. Batra, J. Elast. **13**, 165 (1983).
[3]P. S. Steif, J. Mech. Phys. Solids **31**, 359 (1983).
[4]R. D. Mountain and C. Donald, J. Res. Natl. Bur. Stand. **85**, 109 (1980).
[5]J. H. Weiner, Phys. Rev. B **24**, 845 (1981).
[6]R. F. S. Hearmon, Solid State Commun. **37**, 915 (1981).
[7]E. H. Yotte, Philos. Mag. A **46**, 617 (1982).
[8]C. C. Mathai, P. J. Grout, and N. H. March, J. Phys. Chem. Solids **42**, 317 (1981).
[9]K. P. Thakur and S. Ahmad, in *Proceedings of the Solid State Physics Symposium, Trombay, 1984* (D.A.E., Bombary, 1984), Vol. 27c, p. 240.
[10]M. Born, Proc. Cambridge Philos. Soc. **36**, 160 (1940).
[11]M. Born and R. Fürth, Proc. Cambridge Philos. Soc. **36**, 454 (1940).
[12]M. Born and R. D. Misra, Proc. Cambridge Philos. Soc. **36**, 466 (1940).
[13]R. Fürth, Proc. Cambridge Philos. Soc. **37**, 34;177 (1941).
[14]R. D. Misra, Proc. Cambridge Philos. Soc. **36**, 173 (1940).
[15]N. H. Macmillan and A. Kelly, Proc. R. Soc. London Ser. A **330**, 291 (1972).
[16]N. H. Macmillan and A. Kelly, Proc. R. Soc. London Ser. A **330**, 309 (1972).
[17]N. H. Macmillan and A. Kelly, Mater. Sci. Eng. **12**, 79 (1973).
[18]A. Kelly, *Strong Solids* (Clarendon, Oxford, 1966).
[19]A. Kelly, W. R. Tyson, and A. A. Cottrell, Philos. Mag. **15**, 567 (1967).
[20]A. Kelly, W. R. Tyson, and A. A. Cottrell, Can. J. Phys. **45**, 883 (1967).
[21]K. P. Thakur, Phys. Rev. B **26**, 3001 (1982).
[22]K. P. Thakur, J. Appl. Phys. **53**, 8722 (1982).
[23]S. Ahmad and K. P. Thakur, in Proceedings of the Nuclear Physics and Solid State Physics Symposium, Banaras Hindu University, Varanashi, 1982 (unpublished).