Consequences of crystallographic equivalence between bct and fct indium

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(Received 26 August 1985; revised manuscript received 28 April 1986)

The force-constant relations involving the elastic constants and the phonon dispersion relations for bct indium, deduced on the basis of a general tensor force (GTF) model, are compared with those for fct indium to resolve some conflicting consequences of their crystallographic equivalence. It is shown that the numerical values of the force constants of this model differ from bct indium to fct indium, whereas those of other lattice-dynamical models are invariant, but the same transformation equation relates the phonon frequencies of the former with those of the latter in all cases. Further, the relations between the GTF constants of bct indium and those of fct indium, obtained by making use of their relations with other invariant force constants reveal their correct dependence on coordinate axes. The basic differences between GTF and other models, the transformation properties of these force constants, and their link with the various manifestations of the crystallographic equivalence are discussed.

I. INTRODUCTION

The atomic arrangement of indium could be viewed either as body-centered tetragonal referred to X, Y, and Z axes, or as face-centered tetragonal referred to x, y, and z axes, but the former configuration is related to the latter by a coordinate-axis transformation,[1]

$$\hat{\mathbf{X}}=\tfrac{1}{2}(\hat{\mathbf{x}}+\hat{\mathbf{y}}),\quad \hat{\mathbf{Y}}=\tfrac{1}{2}(\hat{\mathbf{y}}-\hat{\mathbf{x}}),\quad \text{and } \hat{\mathbf{Z}}=\hat{\mathbf{z}}\ , \tag{1}$$

which rotates the x and y axes through 45° about the Z axis. Nevertheless, the crystallographic equivalence between bct and fct lattices has not been understood correctly. For instance, several authors who treated the atomic arrangement of indium as bct have invoked this equivalence with regard to the elastic constants,[2] the Brillouin zone,[3,4] as well as the lattice constants[5] and this misinterpretation has invariably introduced serious errors into the lattice-dynamical calculations on indium. Although Ashokkumar and Sharan[1] were the first to recognize these errors, their calculations, which are in very good agreement with the pseudopotential calculations of Reissland and Ese,[6] did not reveal any of its consequences. Further, Gunton and Saunders,[7] Garrett and Swihart,[8] as well as Chulkov *et al.*[9] studied the lattice dynamics of indium, treating its atomic arrangement as fct, on the basis of model potentials. However, no attempt was made to interpret its crystallographic equivalence with bct indium. On the contrary, the lattice dynamics of indium was investigated on the basis of the De Launay angular force (DAF), the Clark-Gazis-Wallis (CGW), the modified axially symmetric (MAS), and the general tensor force (GTF) models by Ramamurthy and Rajendraprasad,[10–14] who referred its atomic arrangement to bct axes as well as to fct axes and exploited their equivalence to obtain results which are free from any mathematical or numerical errors. Their results are in very good agreement with the phonon frequencies of indium deduced by Garrett and Swihart[8] as well as with their experimental values,[15] but differ significantly from other theoretical studies.[1,6,7,9] In order to understand the crystallographic equivalence and its consequences, it is therefore essential to compare these lattice dynamical studies on bct indium with the corresponding studies on fct indium.

Detailed analysis by the present author of the lattice dynamical data on indium published elsewhere[10–12] reveals that some of these parameters depend on the atomic arrangement, while the others depend on the crystallographic axes. The former are invariant with respect to coordinate-axis transformation (1) and hence are the same for the bct lattice and the fct lattice, whereas the latter differ from bct indium to fct indium. Further, it could be shown that the shape and size of the atomic polyhedron and the Brillouin zone as well as the numerical values of the density and the atomic force constants belong to the former category. On the other hand, the elements of the dynamical matrix, the phonon dispersion relations along the principal symmetry directions, as well as the numerical values of the axial ratio and the elastic constants belong to the latter category, but Eq. (1) ensures that the same phonon frequency distribution function $G(\nu)$, lattice specific heat C_V, and Debye temperature Θ_D are associated with both lattices. Nevertheless, the numerical values of GTF constants, which differ significantly from bct indium to fct indium, together with the apparent invariance, with respect to Eq. (1), of the expressions for most elastic constants, suggest that the above categorization of force constants is not correct. It is therefore of utmost importance to ascertain the origin of this somewhat confusing consequence of the crystallographic equivalence by investigating the lattice dynamics of indium using a GTF model and by relating its force constants with those of other models. This paper describes these investigations which lead to the correct interpretation of the equivalence between bct and fct lattices.

II. THEORY

When the atomic interactions of bct indium are expressed in terms of general tensor forces and their range is extended up to fourth-nearest neighbors, the elements of the dynamical matrix are given by[16]

$$MD_{XX}=4[\lambda_1 S_X^2+\tau_1 S_Y^2+2\lambda_2(1-C_X C_Y C_Z)+\lambda_3(1-C_{2X}C_{2Y})+\lambda_4 S_Z^2]\ , \tag{2}$$

$$MD_{XY}=4[2\nu_2 S_X S_Y C_Z+\nu_3 S_{2X} S_{2Y}]\ , \tag{3}$$

$$MD_{XZ}=8\xi_2 S_X C_Y S_Z\ , \tag{4}$$

and

$$MD_{ZZ}=4[\rho_1(S_X^2+S_Y^2)+2\rho_2(1-C_X C_Y C_Z)+\rho_3(1-C_{2X}C_{2Y})+\rho_4 S_Z^2]\ , \tag{5}$$

where $S_X=\sin(q_X a)$, $S_{2X}=\sin(2q_X a)$, $C_X=\cos(q_X a)$, and $C_{2X}=\cos(2q_X a)$, etc. M is the mass of the ion, $2a$ is the lattice constant along the X direction, and λ_n, τ_n, ν_n, ξ_n, and ρ_n are the nth-neighbor tensor force constants.

On the other hand, corresponding elements of the dynamical matrix for fct indium could be written as[16]

$$MD_{xx}=4[\mu_1(1-C_x C_y)+\mu_2(1-C_x C_z)+\chi_2(1-C_y C_z)+\mu_3 S_x^2+\chi_3 S_y^2+\mu_4 S_z^2]\ , \tag{6}$$

$$MD_{xy}=4\kappa_1 S_x S_y\ , \tag{7}$$

$$MD_{xz}=4\psi_2 S_x S_z\ , \tag{8}$$

and

$$MD_{zz}=4\{\sigma_1(1-C_x C_y)+\sigma_2[2-C_z(C_x+C_y)]+\sigma_3(S_x^2+S_y^2)+\sigma_4 S_z^2\}\ , \tag{9}$$

where $S_x=\sin(q_x a')$, $S_z=\sin(q_z c)$, $C_x=\cos(q_x a')$, and $C_z=\cos(q_z c)$, etc., $2a'$ and $2c$ are the lattice constants along the x and z directions, respectively, and μ_n, χ_n, κ_n, ψ_n, and σ_n are the nth-neighbor tensor force constants.

The 12 force constants that appear in the dynamical matrix elements of indium are evaluated by making use of the experimental values of five zone-boundary frequencies and six elastic constants, in addition to the elastic inconsistency of this model,[13] which gives rise to two different relations for C_{44}. The force-constant expressions for the elastic constants of bct indium and fct indium, obtained by comparing their secular determinants in the long-wavelength limit with the elastic determinant, are listed in Table I, while those for zone-boundary frequencies are not given here. The experimental values of the elastic constants[17] measured on fct indium at 78 K are included in Table I, but those of the zone-boundary frequencies[15] are given in Ref. 16. Corresponding experimental data on bct indium, determined by exploiting the coordinate-axis transformation (1) are given in Ref. 14. However, the numerical values of the force constants of bct indium as well as fct indium, which have been utilized in the calculation of the phonon frequencies at several wave vectors and polarizations are listed in Table II.

III. RESULTS AND DISCUSSION

The phonon frequencies of fct indium deduced on the basis of GTF model are in excellent agreement with the corresponding experimental frequencies along all branches except $T_1[\zeta\zeta 0]$, the former in this region being larger than the latter. But the softness of this mode has not been predicted, so far, by any lattice dynamical calculations other than that of Garrett and Swihart.[8] The dispersion curves of fct indium, obtained by plotting these frequencies as a function of the reduced wave vector ζ along $[\zeta 00]$, $[\zeta 0\zeta]$, $[\zeta\zeta 0]$, and $[00\zeta]$ directions are in no way different from those shown in Figs. 3(a), 3(b), 3(c), and 3(d), respectively, of Ref. 13. In addition, the phonon frequencies of bct indium, calculated by solving the secular determinant of the present GTF model along the $[\zeta\zeta 0]$, $[\zeta\zeta 2\zeta]$, $[\zeta 00]$, and $[00\zeta]$ directions are in very good agreement with their experimental values but differ significantly from those calculated on the basis of an earlier GTF model[2] using correct values of the elastic constants and shown in Fig. 1 of Ref. 14. These frequencies are transformed by means of Eq. (1) and are superimposed on the corresponding dispersion curves of fct indium to facilitate the comparison among them. Notwithstanding the differences in the numerical values of their force constants, these figures (which are not shown here) reveal that the transformed phonon frequencies of bct indium are identical with those of fct indium at all wave vectors and polarizations. Hence, the present investigations establish the fact that the phonon dispersion relations of the GTF model belong to the latter category. On the contrary, the apparent similarities in the expressions for C_{11} and C_{66}, together with the differences in those for C_{13} and C_{44} of the GTF model (see Table I) clearly indicate that the force constants do not belong to the former category.

It is obvious from Table II that the numerical values of the GTF constants of bct indium differ significantly from those of fct indium, even though the range of atomic interactions is restricted to the first four neighbors in both cases and the same set of zone-boundary frequencies and elastic constants which are consistent with Eq. (1) were utilized in their evaluation. In order to ascertain why these force constants are not invariant with respect to the coordinate axes, it is essential to compare them with those of other lattice-dynamical models. For this purpose, the atomic interactions of indium, extended over its unit cell, are expressed in terms of central and angular forces or radial and tangential forces and the same electron-ion interactions are incorporated into all models. The DAF, CGW, and MAS models, so developed, would have, respectively, 8, 11, and 13 force constants, whereas the GTF model, which neglected the electron-ion interactions, has only 12 force constants. These were evaluated by making use of experimental values of zone-boundary frequencies and elastic constants together with an equilibrium condition which must be imposed on force-constant models explicitly to minimize the total potential energy of the crystal. The numerical values of the force constants so obtained in the case of the MAS model,[10] the CGW model,[11,12] and the DAF model[16] for bct indium are identical with those of the corresponding constants for fct in-

TABLE I. Expressions for the elastic constants of indium and their experimental values (in GPa) (Ref. 17).

Axes	bct (axial ratio, p)	fct (axial ratio, t)	
cC_{11}	$(\lambda_1+\lambda_2+2\lambda_3)$	$(\mu_1+\mu_2+2\mu_3)$	52.60
cC_{12}	$2(\nu_2+2\nu_3)-(\tau_1+\lambda_2+2\lambda_3)$	$2\kappa_1-(\mu_1+\chi_2+2\chi_3)$	41.48
cC_{13}	$2p\xi_2-(\rho_1+\rho_2+2\rho_3)$	$2t\psi_2-(\sigma_1+\sigma_2+2\sigma_3)$	44.57
cC_{33}	$p^2(\rho_2+\rho_4)$	$2t^2(\sigma_2+\sigma_4)$	50.80
cC_{44}	$p^2(\lambda_2+\lambda_4)^a$ $(\rho_1+\rho_2+2\rho_3)^b$	$t^2(\mu_2+\chi_2+2\mu_4)^a$ $(\sigma_1+\sigma_2+2\sigma_3)^b$	7.64
cC_{66}	$(\tau_1+\lambda_2+2\lambda_3)$	$(\mu_1+\chi_2+2\chi_3)$	16.96

[a]Along the $[00\zeta]$ direction.
[b]Along the $[\zeta 00]$ direction.

dium, but these are not reproduced here. Nevertheless, the dispersion curves of bct indium do not match those of fct indium in any case. Thus the invariance of these force constants with respect to coordinate axes as well as the transformation of their dispersion curves according to Eq. (1) clearly indicates that the phonon dispersion relations of a model are of no importance in the categorization of its force constants.

The author[18] has shown by resolving the atomic displacements along three mutually perpendicular directions that the force constants of nonequivalent models for any crystal could be interrelated. This procedure was adopted by Ramamurthy and Rajendraprasad to deduce the physically meaningful relations between the force constants of the DAF, CGW, MAS, and GTF models (which express the same atomic interactions, extended up to fourth-nearest neighbors, in a variety of inadequate ways) for fct indium as well as for bct indium, and these are given in Refs. 13 and 16. Further, the invariance of the force constants of the DAF, MAS and CGW models, with respect to the crystallographic axes, is exploited to obtain the following relations between the GTF constants of bct indium and those of fct indium,

$$(1)_{XX}=\lambda_1\equiv(\mu_1+\kappa_1)=(1)_{xx}+(1)_{xy}\ , \tag{10a}$$

$$(1)_{YY}=\tau_1\equiv(\mu_1-\kappa_1)=(1)_{xx}-(1)_{xy}\ , \tag{10b}$$

$$(1)_{ZZ}=\rho_1\equiv\sigma_1=(1)_{zz}\ , \tag{10c}$$

$$(2)_{XX}=\lambda_2\equiv\tfrac{1}{2}(\mu_2+\chi_2)=\tfrac{1}{2}[(2)_{xx}+(2)_{yy}]\ , \tag{11a}$$

$$(2)_{XY}=\nu_2\equiv\tfrac{1}{2}(\mu_2-\chi_2)=\tfrac{1}{2}[(2)_{xx}-[(2)_{yy}]\ , \tag{11b}$$

$$(2)_{XZ}=\xi_2\equiv\frac{1}{\sqrt{2}}\psi_2=\frac{1}{\sqrt{2}}(2)_{xz}\ , \tag{11c}$$

$$(2)_{ZZ}=\rho_2\equiv\sigma_2=(2)_{zz}\ , \tag{11d}$$

$$(3)_{XX}=\lambda_3\equiv\tfrac{1}{2}(\mu_3+\chi_3)=\tfrac{1}{2}[(3)_{xx}+(3)_{yy}]\ , \tag{12a}$$

$$(3)_{XY}=\nu_3\equiv\tfrac{1}{2}(\mu_3-\chi_3)=\tfrac{1}{2}[(3)_{xx}-(3)_{yy}]\ , \tag{12b}$$

$$(3)_{ZZ}=\rho_3\equiv\sigma_3=(3)_{zz}\ , \tag{12c}$$

$$(4)_{XX}=\lambda_4\equiv\mu_4=(4)_{xx}\ , \tag{13a}$$

and

$$(4)_{ZZ}=\rho_4\equiv\sigma_4=(4)_{zz}\ , \tag{13b}$$

where $(n)_{XX}$ and $(n)_{xx}$, etc., are the corresponding elements of the nth-nearest-neighbor tensor force-constant matrix and these have been denoted by equivalent Greek letters in Eqs. (2)–(9) as well as in Tables I and II. Besides, the numerical values of these constants given in Table II are in complete agreement with these relations.

TABLE II. Numerical values of GTF constants (in N m^{-1}).

bct indium		fct indium	
λ_1	14.690	μ_1	7.482
τ_1	0.273	κ_1	7.209
ρ_1	−3.320	σ_1	−3.320
λ_2	1.058	μ_2	4.708
ν_2	3.650	χ_2	−2.592
ξ_2	4.209	ψ_2	5.953
ρ_2	5.437	σ_2	5.437
λ_3	0.020	μ_3	0.393
ν_3	0.373	χ_3	−0.353
ρ_3	−0.116	σ_3	−0.116
λ_4	−0.253	μ_4	−0.253
ρ_4	−0.082	σ_4	−0.082

It should follow from Eqs. (10)–(13) that all GTF constants of bct indium could be transformed to those of fct indium by means of Eq. (1) and hence these investigations establish unequivocally that they belong to the latter category. Further, the analysis of the elastic-constant relations given in Table I reveal that the invariance of C_{11} and C_{66} expressions is destroyed, whereas that of C_{13} and C_{44} expressions is restored by the correct transformation of these force constants. It is therefore obvious that the phonon dispersion relations, expressions for the elastic constants, as well as the force constants of GTF model belong to the same category even though the force constants

of DAF, CGW, and MAS models belong to the other category. Thus the force constants of indium exhibit the most striking consequence of the crystallographic equivalence between bct and fct lattices. It may be recalled in this context that the nature of GTF constants is basically different from that of any other force constants, notwithstanding the degree of equivalence that exists between them. In general, the second derivative of the potential energy of a crystal with respect to atomic displacements, taken at the equilibrium separation between two atoms, is a tensor of second rank which could be represented by a 3×3 matrix. Most lattice-dynamical models make use of some arbitrary assumptions regarding the nature of atomic interactions while the GTF model exploits the symmetry elements associated with the crystal structure, to reduce the number of independent parameters associated with each set of nearest neighbors. As a consequence, the central and angular force constants of DAF and CGW models as well as the radial and tangential force constants of MAS model become scalar quantities whereas the GTF constants retain the characteristics of second-rank tensor. However, the intrinsic differences in the transformation properties of the former and the latter manifest themselves when the crystallographic equivalence between bct indium and fct indium is invoked.

The crystallographic-axis transformation which rotates the x and y axes through 45° about the Z axis is represented by a 3×3 orthogonal matrix R. In view of the fact that this transformation corresponds to Eq. (1), the matrix R transforms the fct lattice to the bct lattice. The force constants of DAF, CGW, and MAS models, being scalar quantities, are invariant with respect to R. On the other hand, the GTF constants of bct indium are related to those of fct indium by a similarity transformation involving R. The matrices representing the corresponding tensors associated with first-, second-, third-, and fourth-nearest neighbors of indium are given in Ref. 16. It can be shown by making use of R, and its inverse that the similarity transformations reduce these matrices, respectively, to Equations (10), (11), (12), and (13). Hence, the relations between the GTF constants of bct indium and fct indium obtained by making use of their transformation properties are identical with those deduced by exploiting their equivalence with other invariant force constants. However, it is necessary to emphasize that the lattice-dynamical studies of most solids are confined to single set of coordinate axes which is invariably linked with the corresponding lattice symmetry. The force constants of different models for any solid could be related with those of GTF model.[13,16] Under these circumstances, crystallographic equivalence between bct lattice and fct lattice has played a useful role in demonstrating the uniqueness of GTF constants. Moreover, the correct interpretation of this equivalence is of utmost importance in any lattice-dynamical study of indium and white tin.

ACKNOWLEDGMENTS

The author is most grateful to Dr. H. G. Smith of Oak Ridge National Laboratory for sending the unpublished experimental data on phonon frequencies of indium and to Dr. S. B. Rajendraprasad for many valuable and stimulating discussions as well as for his assistance in computing the numerical values of the force constants.

[1]Ashokkumar and B. Sharan, J. Phys. C **5**, 3161 (1972).
[2]L. J. Slutsky and A. Livingston, J. Chem. Phys. **32**, 1093 (1960).
[3]B. Sharan and R. P. Bajpai, J. Phys. Soc. Jpn. **26**, 1359 (1969).
[4]B. Sharan and R. P. Bajpai, Indian J. Pure Appl. Phys. **8**, 331 (1970).
[5]P. Joardar and S. Chakraborty, Indian J. Pure Appl. Phys. **17**, 794 (1979).
[6]J. A. Reissland and O. Ese, J. Phys. F **5**, 110 (1975).
[7]D. J. Gunton and G. A. Saunders, Solid State Commun. **12**, 569 (1973).
[8]D. G. Garrett and J. C. Swihart, J. Phys. F **6**, 1781 (1976).
[9]E. V. Chulkov, S. G. Psakhe, M. F. Zhorovkov, and V. E. Panin, Fiz. Met. Metalloved. **49**, 1127 (1980).
[10]V. Ramamurthy and S. B. Rajendraprasad, J. Phys. F **11**, 2275 (1981).
[11]V. Ramamurthy and S. B. Rajendraprasad, Pramana **19**, 435 (1982).
[12]V. Ramamurthy and S. B. Rajendraprasad, Can. J. Phys. **61**, 58 (1983).
[13]V. Ramamurthy and S. B. Rajendraprasad, Pramana **25**, 603 (1985).
[14]V. Ramamurthy and S. B. Rajendraprasad, J. Phys. Chem. Solids **47**, (1986) (unpublished).
[15]W. Reichardt and H. G. Smith (unpublished).
[16]S. B. Rajendraprasad, Ph.D. thesis, Indian Institute of Technology, Delhi, 1982.
[17]B. S. Chandrasekhar and J. A. Rayne, Phys. Rev. **124**, 1011 (1961).
[18]V. Ramamurthy, Phys. Status Solidi B **112**, 463 (1982).