

Band-structure perturbations in strained crystals

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A perturbation method has been developed in the modified-plane-wave formalism to calculate first-order splitting and shifting of electronic energy levels for fcc crystals under hydrostatic, tetragonal, and trigonal strains. Numerical results for Cu for the Γ , X , and L symmetry points are given. The hydrostatic results are compared with the difference calculation of Davis *et al.* The tetragonal and trigonal results are compared with those of Juras and Segall who performed both a perturbation and a difference calculation. Reasonable agreement with these other calculations is obtained. For the shear cases the numerical ratios of appropriate shifts are in excellent agreement with the ratios predicted from symmetry calculations alone. A representative case involving a second-order correction due to mixing between close-lying levels is included.

I. INTRODUCTION

A useful check on the crystal potential used in an electronic band-structure calculation may be obtained from a first-principles determination of deformation potentials if these can be checked against experimentally determined values. Deformation potentials are also pertinent to electron-phonon calculations for long-wavelength phonons.

For transition elements, or compounds containing a transition element, a shear strain may change the connectivity of energy bands near the Fermi energy, thus causing changes in the Fermi-surface shape and associated physical properties.

In the present paper a perturbation approach has been incorporated into a modified-plane-wave (MPW) band-structure computer program¹ so that, in addition to generating energy values at symmetry points in the Brillouin zone, deformation potentials at these points can be generated for hydrostatic, tetragonal, or trigonal strains.² Preliminary calculations have been performed for copper because tabulations of the crystal potential are readily available.^{3,4}

The MPW formalism⁵ is a variational procedure in which the trial expansion functions [the ϕ_i of Eq. (1)] are symmetrized atomiclike functions (ALF's) and symmetrized plane waves:

$$\psi_n(\vec{r}) = \sum_i c_i^n \phi_i(\vec{r}) . \quad (1)$$

In the present calculation a muffin-tin potential is used; like the orthogonalized-plane-wave (OPW) formalism, this method is suitable for a more general form of potential.⁶ In the MPW formalism the perturbation calculation can be put in a quite

tractable form; ALF's of the unperturbed crystal may be retained as expansion functions.

Under hydrostatic strain the energy shifts can be expressed as a linear combination of two terms; one due explicitly to the change in lattice parameter, the other due to the change in crystal potential within a unit cell.⁷ Since there is no change in symmetry the degeneracies remain unchanged.

In the pure-shear case it is assumed that, to first order, the perturbation does not change the crystal potential within a unit cell^{8,9}; i. e., band-structure shifts and splittings of degeneracies are due solely to the changes in symmetry and lattice parameters.

The strains under consideration are of the order 10^{-4} , producing band shifts of order 10^{-4} Ry, near the precision limit of most current band-structure calculations. A perturbation approach is preferable in this range. Such an approach also saves computer time by avoiding recalculation of the band-structure with new lattice constants. The algebraic expressions for the deformation potentials may eventually furnish some physical insight into the effects of strain deformation.

II. PERTURBATION PROCEDURE

In the present formulation the plane wave ϕ_i 's themselves change as stress is applied (due to these terms containing the lattice constant explicitly). Thus, the usual perturbation expression

$$\Delta E = \langle \psi^0 | H_{\text{pert}} | \psi^0 \rangle \quad (2)$$

is replaced by

$$\Delta E_n = \langle \vec{c}^{0,n} | \underline{\Delta H} - E_n^0 \underline{\Delta S} | \vec{c}^{0,n} \rangle , \quad (3)$$

with

$$\Delta H_{ij} = H_{ij}^1 - H_{ij}^0, \quad (4)$$

$$H_{ij}^0 \equiv \langle \phi_i^0 | -\nabla^2 + V^0(r) | \phi_j^0 \rangle, \quad S_{ij}^0 \equiv \langle \phi_i^0 | \phi_j^0 \rangle, \quad (5)$$

$$H_{ij}^1 \equiv \langle \phi_i | -\nabla^2 + V^0(r) + \Delta V(r) | \phi_j \rangle. \quad (6)$$

In Eq. (5) integration is over the original undeformed crystal; in Eq. (6) integration is over the deformed crystal. ΔS_{ij} is defined analogously to ΔH_{ij} . Equation (3) is derived in Appendix A.

Three comments concerning these equations are in order: (i) ΔH_{ij} (ΔS_{ij}) is obtained algebraically by expanding H_{ij}^1 (S_{ij}^1) in a Taylor series. (ii) In the present formulation both H_{ij}^1 , S_{ij}^1 and H_{ij}^0 , S_{ij}^0 must be expressed in the lower (tetragonal or trigonal) symmetry for these two cases which change the crystal symmetry. (iii) As discussed above, $\Delta V(r)$ is zero for tetragonal and trigonal strains which preserve the unit cell volume.

Since tetragonal and trigonal strains break the original cubic symmetry, the degeneracy of the unperturbed levels may be lifted by the perturbation. This degeneracy presents no problem, however, since the numerical calculation is formulated in terms of the lower symmetry. Stated differently, use of the irreducible representations of the lower symmetry automatically selects the "correct linear combination" of the original degenerate eigenfunctions. Care is required, however, for nearly degenerate levels which are associated with the same irreducible representation of the lower symmetry. For example, in Cu there are two X_2 and X_5 levels separated by only about 0.01 Ry; under trigonal strain one of the two trigonal D representations compatible with X_5 is also compatible with X_2 so that there can be "mixing" between the original X_2 and X_5 levels. To a good approximation¹⁰ this mixing adds an additional shift,

$$\Delta^{(2)} E \approx \pm (\Delta E_A)^2 / (E_n^0 - E_m^0), \quad (7)$$

where

$$\Delta E_A \equiv \langle \tilde{c}^{0,n} | \underline{\Delta H} - E_A \underline{\Delta S} | \tilde{c}^{0,m} \rangle, \quad (8)$$

$$E_A \equiv (E_n^0 + E_m^0) / 2, \quad (9)$$

and $\underline{\Delta H}$ and $\underline{\Delta S}$ are as defined in Eqs. (4)–(6).

III. NUMERICAL COMPUTATION

For hydrostatic strain, the irreducible representations used are simply those of the cubic group. For tetragonal/trigonal strains compatibility tables are used to determine which tetragonal/trigonal representations are compatible with the cubic representation for the level in question. (Compatibility tables for the Γ , X , and L points are given in Appendix B.) The appropriate symmetrized plane waves and ALF's are then determined and an " E^0 " band-structure calculation is made. For computational convenience the appropriate ΔH_{ij} and ΔS_{ij} integrals are evaluated in the

same section of the computer program where the corresponding H_{ij} and S_{ij} integrals are formed. (Explicit ΔS_{ij} and ΔH_{ij} expressions for hydrostatic, tetragonal, and trigonal strains are given in Appendix C.) These ΔH_{ij} and ΔS_{ij} integrals are stored while the E_n^0 and $c_i^{0,n}$ are determined variationally. Equation (3) is then evaluated giving ΔE_n .

IV. NUMERICAL RESULTS

Results of computer calculations for the symmetry points Γ , X and L of copper for the hydrostatic, tetragonal, and trigonal cases are given in Tables I, II, and III, respectively. Energy shifts for X_2 and X_5 (under trigonal strain) including mixing between levels are listed in Table IV. Strain components are as defined by Juras and Segall.⁸ This corresponds to Kittel's¹¹ notation except for the trigonal case where Kittel's $\frac{1}{2}e$ is replaced by e . The $V^0(r)$ potential used in all calculations in the present work is a slightly modified version of the Chodorow³ potential. (This modification causes the E^0 levels calculated here to differ slightly¹² from those calculated by Burdick.¹³) The $\Delta V(r)$ used for the hydrostatic case is taken from Davis *et al.*⁴; they did not use the Chodorow potential but generated strain-dependent potentials. The shifts computed by Davis *et al.* are given in Table I for comparison.

For the tetragonal case ΔE has been computed for Γ , $X(z)$, $X(x)$, and $L(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. Since a tetragonal strain which singles out the z axis was chosen, $X(x) = X(y) \neq X(z)$. For the trigonal case ΔE has been computed for Γ , X , $L(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, and $L(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. Since the trigonal strain is chosen to be along the $[111]$ axis,

TABLE I. Shifts in energy for some high-symmetry states of Cu for hydrostatic strain ($e = \Delta a/a_0 = -0.005$). Shifts calculated by Davis *et al.* are given in column five for comparison. All energies are in Ry.

State ^a	E^0	ΔE Perturbation	ΔE	
			by differences (present work)	by differences ^b
Γ_{12}	-0.5621	-0.0020		-0.0028
$\Gamma_{25'}$	-0.6233	-0.0035		-0.0042
Γ_1	-1.0497	-0.0109	-0.0103	-0.0097
X_4'	-0.2337	-0.0032	-0.0032	-0.0018
X_5	-0.5053	-0.0010	-0.0009	-0.0016
X_2	-0.5207	-0.0013		-0.0019
L_1^u	-0.0919	0.0045	0.0044	0.0046
L_2'	-0.4289	-0.0058	-0.0056	-0.0046
L_3^u	-0.5150	-0.0013	-0.0012	-0.0019
L_3^l	-0.6270	-0.0037	-0.0036	-0.0043
L_1^l	-0.7654	-0.0075	-0.0075	-0.0071

^aBSW labels (Ref. 22). The superscripts u and l indicate upper and lower levels, respectively.

^bReference 4.

TABLE II. Deformation potentials of some Γ , X , L states of Cu for tetragonal strain calculated by perturbation theory. Shifts calculated by Juras and Segall are given in column five for comparison. Ratios predicted by the Wigner-Eckart theorem are given in column six. All energy entries are in Ry.

Unstrained ^a state	Strained ^b state	E^0	Deformation potentials in Ry per unit strain		Predicted ratio
			This work	Juras and Segall ^c	
Γ_{12}	Γ_1	-0.5621	-0.2716	-0.2740	-b
	I_2	-0.5621	0.2716	0.2740	b
$\Gamma_{25'}$	Γ_3	-0.6233	-0.3188	-0.3400	-2b
	$\Gamma_5(D_{11})$	-0.6233	0.1594	0.1700	b
	$\Gamma_5(D_{22})$	-0.6233	0.1594	0.1700	b
Γ_1	Γ_1	-1.0468	0.0000		0
$X_{4'}$	$Z_{4'}$	-0.2339	-1.5901	-1.6533	-2b
	$X_{3'}$	-0.2339	0.7951		b
X_5	$Z_5(D_{11})$	-0.5056	-0.0282	-0.0410	-b
	$Z_5(D_{22})$	-0.5056	-0.0282	-0.0410	-b
	X_4	-0.5056	0.1981		sum
	X_2	-0.5056	-0.1699		-b
X_2	Z_2	-0.5180	0.0248	0.0110	2b
	X_1	-0.5180	-0.0124		-b
X_3	Z_3	-0.7275	0.0728	0.0500	2b
	X_3	-0.7275	-0.0364		-b
X_1	Z_1	-0.7633	-0.0474	-0.0420	-2b
	X_1	-0.7633	0.0237		b
L_1^{\ddagger}	N_1	-0.0854	0.0000	0.0000	0
$L_{2'}$	N_4	-0.4290	0.0000	0.0000	0
L_3^{\ddagger}	N_1	-0.5096	0.1032	0.1210*	b
	N_2	-0.5096	-0.1032	-0.1210*	-b
L_3^{\ddagger}	N_1	-0.6221	-0.2547	-0.2678*	-b
	N_2	-0.6221	0.2547	0.2678*	b
L_1^{\ddagger}	N_1	-0.7605	0.0000	0.0000	0

^aBSW labels (Ref. 22).

^bTetragonal Γ_i and $Z_i(001)$ equal X_i of BSW. $X(100)$ and N are defined in Tables VI and VII, respectively.

^cThe values marked with an asterisk are from Ref. 9; the rest are from Ref. 8.

$$L(\frac{1}{2} \frac{1}{2} \frac{1}{2}) = L(\frac{1}{2} \frac{1}{2} \frac{1}{2}) = L(\frac{1}{2} \frac{1}{2} \frac{1}{2}) \neq L(\frac{1}{2} \frac{1}{2} \frac{1}{2}) .$$

From Tables II and III it can readily be seen that the numerical calculations satisfy the predicted ratios (see Sec. V) excellently.¹⁴ For comparison, the ΔE values obtained by Juras and Segall^{8,9} using a Green's function method are included in Tables II-IV; agreement between the present values and theirs is reasonably good.¹⁵ For a discussion of the limited experimental data available see Refs. 8 and 9.

TABLE IV. Energy shifts for the X_2 and X_5 representations of Cu for trigonal strain calculated by perturbation theory. The values computed by Juras and Segall are included for comparison. Columns four and six give the first-order shift; columns five and seven give the second-order shift (due to mixing between levels). All energy entries are in Ry for $e = 0.001$.

Unstrained state	Strained state	E^0	Present work		Juras and Segall ^a	
			First order	Second order	First order	Second order
X_5	D_2	-0.4966	-5.0×10^{-6}	3.9×10^{-6}	-0.6×10^{-6}	10.3×10^{-6}
X_2	D_2	-0.5128	0.0	-3.9×10^{-6}		

^aReference 8.

TABLE III. Deformation potentials of some Γ , X , L states of Cu for trigonal strain calculated by perturbation theory. Shifts calculated by Juras and Segall are given in column five for comparison. Ratios predicted by the Wigner-Eckart theorem are given in column six. All energy entries are in Ry.

Unstrained ^a state	Strained ^b state	E^0	Deformation potentials in Ry per unit strain		Predicted ratio
			This work	Juras and Segall ^c	
Γ_{12}	$\Gamma_3(D_{11})$	-0.5618	0.0000	0.0000	0
	$\Gamma_3(D_{22})$	-0.5618	0.0000	0.0000	0
$\Gamma_{25'}$	Γ_1	-0.6230	-0.8394	-0.8262	-2b
	$\Gamma_3(D_{11})$	-0.6230	0.4196	0.4131	b
	$\Gamma_3(D_{22})$	-0.6230	0.4196	0.4131	b
Γ_1	Γ_1	-1.0461	0.0000		0
X_5	D_1	-0.4966	0.0050	0.0006	b
	D_2	-0.4966	-0.0050 ^d	-0.0006 ^d	-b
X_2	D_2	-0.5128	0.0000 ^d	0.0000 ^d	0
	L_1^{\ddagger}	L_1	-0.0854	-2.9930	-3.1355
A_1		-0.0854	0.9976		b
$L_{2'}$	$L_{2'}$	-0.4290	-2.2808	-2.3434	-3b
	A_1	-0.4290	0.7602		b
L_3^{\ddagger}	$L_3(D_{11})$	-0.5096	-0.1580	-0.2550*	- $\frac{1}{2}b$
	$L_3(D_{22})$	-0.5096	-0.1580	-0.2550*	- $\frac{1}{2}b$
	A_1	-0.5096	-0.2558	-0.2901*	sum
	A_2	-0.5096	0.3612	0.4601*	$\frac{1}{2}b$
L_3^{\ddagger}	$L_3(D_{11})$	-0.6221	0.2844	0.2369*	$\frac{1}{2}b$
	$L_3(D_{22})$	-0.6221	0.2844	0.2369*	$\frac{1}{2}b$
	A_1	-0.6221	-0.7342	-0.7488*	sum
	A_2	-0.6221	0.5446	0.5930*	$\frac{1}{2}b$
L_1^{\ddagger}	L_1	-0.7605	-0.1724	-0.1950	-3b
	A_1	-0.7605	0.0574		b

^aBSW labels (Ref. 22).

^bTrigonal Γ_i and $L_i(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ equal L_i of BSW. D and $A(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ are defined in Table VII.

^cReferences 8 and 9. The values marked with an asterisk are from Ref. 9; the rest are from Ref. 8.

^dThis includes first-order terms only.

V. SYMMETRY CONSIDERATIONS

It is well known that a number of predictions can be made from symmetry considerations alone. These predictions allow an "economy of computation" and/or may serve as a check on the numerical computation.

The simplest prediction that can be made from symmetry alone concerns degeneracies. If a three-dimensional cubic representation is compatible with both a one-dimensional and a two-dimensional tetragonal representation, for example, and if there is any energy shift due to the perturbation, then the associated threefold degenerate

level will split into a nondegenerate level and a twofold degenerate level.

The Wigner-Eckart matrix-element theorem¹⁶ can be used to predict the ratios of these splittings. The theorem may be stated in the form¹⁷

$$\langle \psi_{\alpha,i} | O_{\gamma,k} | \psi_{\alpha,j} \rangle = F(g, \psi, O, \alpha, \gamma) \langle g_{\alpha,i} | g_{\gamma,k} | g_{\alpha,j} \rangle, \quad (10)$$

where α and γ label representations and i, j , and k label "rows" of representations; the $g_{\alpha,i}$ are a set of "partner" functions, as are the $\psi_{\alpha,i}$. The important point is that the numerical factor F is independent of the row labels; thus, by using simple standard functions (like x, y, z or yz, xz, xy , etc.) for the $g_{\alpha,i}$ and $g_{\gamma,k}$, one may quickly calculate ratios such as

$$\langle \psi_{\alpha,1} | O_{\gamma,k} | \psi_{\alpha,1} \rangle / \langle \psi_{\alpha,2} | O_{\gamma,k} | \psi_{\alpha,2} \rangle.$$

It is not necessary to know the $\psi_{\alpha,i}$ and $O_{\gamma,k}$ explicitly; their transformation properties are sufficient. The applicability of the Wigner-Eckart theorem to the present perturbation formulation is shown in Appendix D.

Once the symmetry of the "equivalent operator" has been established (Appendix D), standard tables may be used (or readily constructed) to give the various splitting ratios. It is found, for example, that for the tetragonal case, the twofold degenerate level $X_5(z)$ remains degenerate and has a shift which is exactly balanced by the net shifts associated with the splitting of the equivalent levels on the x and y axes of \mathbf{k} space, i. e., $X_5(x)$ and $X_5(y)$.

The previous example is part of a more general result; from symmetry considerations alone the net first-order level shift for a given type of \mathbf{k} point must be zero for strains that preserve cell volume. The argument is as follows: For a tetragonal strain which singles out the z axis the "equivalent" perturbing Hamiltonian has symmetry properties represented by the function $2z^2 - x^2 - y^2$, as shown in Appendix D. If the x axis were singled out the corresponding function would be $2x^2 - y^2 - z^2$; for the y axis, $2y^2 - z^2 - x^2$. If all three strains were applied the net shift would be associated with an operator represented by the sum of the three functions listed; since this sum is zero, the net shift for all three strains at any \mathbf{k} point must be zero, and thus the net shift for all \mathbf{k} points of a particular type must be zero. This implies that the net shift for all \mathbf{k} points of a given type, for any one of the three strains above, must be zero, since, due to the original cubic symmetry, the net shift with z unique cannot differ from the net shift with x or y unique. A similar argument holds for trigonal strain.

For the Γ point, or any point of $\bar{\mathbf{k}}$ space such that

all independent points of the same "type" must behave identically due to symmetry (such as L under tetragonal strain, for example), one can use this "center-of-gravity preservation," in conjunction with compatibility (Appendix B), to predict ratios of energy shifts, thus dispensing with the matrix-element theorem for these points.

For symmetry points *not* satisfying the above conditions (e. g., X under tetragonal strain, L under trigonal strain) the matrix-element theorem provides more information than one obtains from the combination of compatibility and center-of-gravity preservation. For example, under tetragonal strain compatibility shows (see Table V and accompanying text) that $X_5(z)$ does not split and that $X_5(x)$ and $X_5(y)$ each split into two levels. This information, combined with the net zero shift for the set of three independent X points, cannot distinguish between case I, in which $X_5(z)$ does not shift while $X_5(x)$ and $X_5(y)$ each split *evenly*, and case II, in which $X_5(x)$ and $X_5(y)$ each split *unevenly* while $X_5(z)$ shifts just enough to cancel the net $X_5(x)$ and $X_5(y)$ shifts. The matrix-element theorem does distinguish and predicts case II.

VI. SUMMARY AND CONCLUSIONS

First-order energy shifts and splittings for several symmetry points in the Brillouin zone of copper under hydrostatic, tetragonal, and trigonal strain are listed in Tables I, II, and III, respectively; the shear results are tabulated in the form of deformation potentials. Second-order results for a representative case are tabulated in Table IV. The perturbation and difference calculations for the hydrostatic case with $e = -0.005$ are in good agreement. The Γ_1 level shows the largest shift of those listed. Agreement with the difference calculations of Davis, Faulkner, and Joy⁴ (DFJ) seems reasonable, considering that the two calculations were performed with different crystal potentials, only the change in potential being the same for both. The largest discrepancy between the present results and the DFJ calculation is for the X_4 shift.

The calculated shear shifts and splittings are consistent with the ratios predicted from symmetry considerations alone. Most of these results also show good agreement with those of Juras and Segall^{8,9}; differences may be due in part to the slight difference in potentials between the two calculations.¹⁵ Under pure shear the Γ_1 level does not shift. For tetragonal shear the $X_4(z)$ level shows the largest deformation potential (of those listed); again, the largest discrepancy between the two sets of calculations occurs for this level. For trigonal shear the L_1^u level has the largest deformation potential (of those listed) and also shows the largest discrepancy between the two sets of calculations.

Second-order effects for the $X_5 - X_2$ interaction differ from the Juras-Segall results.¹⁸

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APPENDIX A: DERIVATION OF EQ. (3) OF TEXT

In matrix form the Schrödinger equation may be written

$$\underline{M}\vec{c} = 0, \quad (\text{A1})$$

with

$$\underline{M} = \underline{H} - E\underline{S}. \quad (\text{A2})$$

For the strained crystal Eq. (A1) becomes

$$(\underline{M} + \underline{\Delta M})(\vec{c} + \underline{\Delta}\vec{c}) = 0. \quad (\text{A3})$$

Keeping first-order terms and multiplying by \vec{c}^* , one obtains

$$\langle \vec{c} | \underline{\Delta M} | \vec{c} \rangle = 0. \quad (\text{A4})$$

since $\sum_i c_i^* M_{ij} = 0$ from the Hermiticity of \underline{M} . From Eq. (A2),

$$\underline{\Delta M} = \underline{\Delta H} - E^0 \underline{\Delta S} - S^0 \underline{\Delta E} \quad (\text{A5})$$

Substituting Eq. (A5) into (A4) and using $\langle \vec{c} | S^0 | \vec{c} \rangle = 1$, one obtains Eq. (3) of the main text.

APPENDIX B: COMPATIBILITY RELATIONS

A. fcc-bct

Considering the body-centered tetragonal¹⁹ (bct) structure (D_{4h}^{17}) as a deformation²⁰ of the fcc structure (O_h^5), compatibility tables are constructed, in the sense of Parmenter,²¹ showing how various irreducible representations of the point groups of O_h^5 transform into those of D_{4h}^{17} (Table V). The tetragonal strain used in this paper singles out the z axis; for this case the irreducible bct representations for $Z(001)$ after deformation are identical to the corresponding fcc representations for $X(001)$ before deformation. (The x, y , and z axes used in this Appendix are those of the original fcc lattice.)

In Table V the labeling of the representations listed under O_h^5 is that of Bouckaert *et al.*²² (BSW); Γ_i of D_{4h}^{17} equals X_i of BSW; X_i and N_i of D_{4h}^{17} are defined in Tables VI and VII, respectively.

B. fcc-trigonal (Ref. 23)

As in the tetragonal case, compatibility tables are constructed showing how various irreducible representations of the point groups of O_h^5 transform into those of D_{3d}^5 (Table VIII). The trigonal strain used in this paper singles out the $[111]$ axis; for this case the irreducible trigonal representations for $L(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ after deformation are identical to the

TABLE V. Compatibility relations for the representations of various point groups connecting the bct structure (D_{4h}^{17}) with the fcc structure (O_h^5). See text for explanation of notation.

O_h^5	D_{4h}^{17}	O_h^5	D_{4h}^{17}
Γ_1	Γ_1	X_4	X_3
Γ_2	Γ_2	X_5	X_2 X_4
Γ_{12}	Γ_1 Γ_2	$X_{1'}$	etc. $X_{1'}$
$\Gamma_{15'}$	Γ_4 Γ_5		
$\Gamma_{25'}$	Γ_3 Γ_5	L_1 L_2	N_1 N_2
$\Gamma_{1'}$	etc. $\Gamma_{1'}$	L_3	N_1 N_2
$X_1(100)$	X_1	$L_{1'}$	N_3
X_2	X_1	$L_{2'}$	N_4
X_3	X_3	$L_{3'}$	N_3 N_4

TABLE VI. Character table for $X(100)$ of D_{4h}^{17} . For $X_{1'}$, X_4 , the character for R equals that of the corresponding unprimed representation; the character for JR is the negative of that for the corresponding R .

	E	$C_4^2(x)$	$C_4^2(y)$	$C_4^2(z)$	J	$JC_4^2(x)$	$JC_4^2(y)$	$JC_4^2(z)$
X_1	1	1	1	1	1	1	1	1
X_2	1	-1	1	-1	1	-1	1	-1
X_3	1	1	-1	-1	1	1	-1	-1
X_4	1	-1	-1	1	1	-1	-1	1

TABLE VII. Character table for N of D_{4h}^{17} . (This table is also valid for A and D of D_{3d}^5 .)

	E	C_2	J	JC_2
N_1	1	1	1	1
N_2	1	-1	1	-1
N_3	1	1	-1	-1
N_4	1	-1	-1	1

TABLE VIII. Compatibility relations for the representations of various point groups connecting the trigonal structure (D_{3d}^5) with the fcc structure (O_h^5). See text for explanation of notation.

O_h^5	D_{3d}^5	O_h^5	D_{3d}^5
Γ_1	Γ_1	X_1	D_3
Γ_2	Γ_2	X_2	D_4
Γ_{12}	Γ_3	X_3	D_3
$\Gamma_{15'}$	Γ_2 Γ_3	X_4	D_4
$\Gamma_{25'}$	Γ_1 Γ_3	X_5	D_3 D_4
$\Gamma_{1'}$ etc.	$\Gamma_{1'}$	$L_1(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ L_2	A_1 A_2
X_1	D_1	L_3	A_1 A_2
X_2	D_2	$L_{1'}$	A_3
X_3	D_1	$L_{2'}$	A_4
X_4	D_2		
X_5	D_1 D_2	$L_{3'}$	A_3 A_4

corresponding fcc representations before deformation. In Table VIII the labeling of the representations listed under O_h^5 is that of BSW; Γ_i of D_{3d}^5 equals L_i of BSW; D_i and A_i are identical to N_i of Table VII.

APPENDIX C: EXPLICIT FIRST-ORDER ΔS_{ij} AND ΔH_{ij} EXPRESSIONS FOR HYDROSTATIC, TETRAGONAL, AND TRIGONAL STRAINS

A. Definitions

The Y_q are cubic harmonics ($Y_1=1$, $Y_2=z/r$, etc.). Ω is the volume of the primitive cell and $\Delta\Omega$ its change under strain; s is the radius of the muffin-tin sphere. $\Delta V(r)$ is the change in the muffin-tin potential; $\Delta\bar{V}$ is the change in potential in the "interstitial" region. For pure shear it is assumed that $\Delta V(r)=\Delta\bar{V}=0$. For symmetrization, g is the number of elements in the group of \vec{k} , h is the dimensionality of the representation, and the D_{11} 's are irreducible representation matrix elements.

B. Basis functions in the MPW method

The trial wave function used in the variational procedure is given by Eq. (1) of the main text. An unsymmetrized ALF has the form

$$i^l [u_{nl}(r)/r] Y_q(\vec{r}/r),$$

where $u_{nl}(r)/r$ is the radial part of the atomic function adjusted to approach zero with zero slope at $r \leq s$. The symmetrized ALF takes on the form

$$\frac{h}{g} i^l \left(\frac{u_{nl}(r)}{r} \right) \sum_R D_{11}(R) P_R Y_q \left(\frac{\vec{r}}{r} \right).$$

The sum on R runs over all operations of the group. Symmetrized plane waves have the form

$$\frac{h}{g} \sum_R D_{11}(R) \exp(iR\vec{k}_j \cdot \vec{r}),$$

where

$$\vec{k}_j \equiv \vec{k} + \vec{K}_j$$

The \vec{K}_j are reciprocal-lattice vectors.

C. ALF-ALF elements

$$\Delta S_{ij} = 0, \quad (C1)$$

$$\Delta H_{ij} = A_{qq} \int_0^s u_{nl}(r) \Delta V(r) u_{n'l}(r) dr, \quad (C2)$$

where

$$A_{qq} \equiv \frac{h}{4\pi g} \int_0^{2\pi} \int_{-1}^1 Y_q \left(\frac{\vec{r}}{r} \right) \sum_R D_{11}(R) P_R Y_q \left(\frac{\vec{r}}{r} \right) d(\cos\theta) d\phi.$$

D. ALF-plane-wave elements

$$\Delta S_{ij} = \frac{h}{g} \sum_R D_{11}(R) \left[\Delta J_{nl} P_R Y_q \left(\frac{\vec{k}_j}{k_j} \right) + J_{nl} P_R \Delta Y_q \left(\frac{\vec{k}_j}{k_j} \right) \right], \quad (C3)$$

where

$$J_{nl} \equiv \int_0^s u_{nl}(r) j_l(k_j r) r dr,$$

$$\Delta J_{nl} = \int_0^s u_{nl}(r) \Delta j_l(k_j r) r dr,$$

$$\Delta j_l(k_j r) = (1/k_j^2) (\vec{k}_j \cdot \Delta \vec{k}_j) [l j_l(k_j r) - k_j r j_{l+1}(k_j r)],$$

$$\Delta Y_q \equiv \left(\frac{\partial Y_q}{\partial k_{jx}} \right) \Delta k_{jx} + \left(\frac{\partial Y_q}{\partial k_{jy}} \right) \Delta k_{jy} + \left(\frac{\partial Y_q}{\partial k_{jz}} \right) \Delta k_{jz}.$$

(For the hydrostatic case $\Delta Y_q = 0$.)

$$\Delta H_{ij} = 2(\vec{k}_j \cdot \Delta \vec{k}_j) S_{ij}^0 + k_j^2 \Delta S_{ij} + G, \quad (C4)$$

where

$$G \equiv \frac{h}{g} \sum_R D_{11}(R) (\Delta B_{nl} P_R Y_q + B_{nl} P_R \Delta Y_q),$$

with

$$B_{nl} \equiv \int_0^s u_{nl}(r) j_l(k_j r) V^0(r) r dr,$$

$$\Delta B_{nl} = \int_0^s u_{nl}(r) \Delta j_l(k_j r) V^0(r) r dr + \int_0^s u_{nl}(r) j_l(k_j r) \Delta V(r) r dr.$$

E. Plane-wave-plane-wave elements

$$\Delta S_{ij} = (\Delta\Omega/\Omega) S_{ij}^0, \quad (C5)$$

with

$$S_{ij}^0 = \frac{\hbar\Omega}{4\pi g} \sum_R D_{11}(R) \delta(\vec{k}_i, R^{-1}\vec{k}_j) .$$

$$\Delta H_{ij} = (\Delta\bar{V} + 2\vec{k}_j \cdot \Delta\vec{k}_j) S_{ij}^0 + (\bar{V} + k_j^2) \Delta S_{ij} + \frac{\hbar}{g} \sum_R D_{11}(R) [Q_1 + Q_2] , \quad (C6)$$

where

$$Q_1 \equiv \int_0^s [\Delta V(r) - \Delta\bar{V}] j_0(Kr) r^2 dr ,$$

$$Q_2 \equiv \int_0^s [V^0(r) - \bar{V}^0] \Delta j_0(Kr) r^2 dr ,$$

$$\Delta j_0(Kr) = - (r/K) (\vec{K} \cdot \Delta\vec{K}) j_1(Kr) ,$$

and

$$\vec{K} \equiv R^{-1} \vec{k}_j - \vec{k}_i .$$

Note that

$$\vec{k}_j \cdot \Delta\vec{k}_j = -ek_j^2 , \quad \text{hydrostatic case}$$

$$= -e(2k_{jz}^2 - k_{jx}^2 - k_{jy}^2) , \quad \text{tetragonal case}$$

$$= -2e(k_{jx}k_{jy} + k_{jx}k_{jz} + k_{jy}k_{jz}) , \quad \text{trigonal case.}$$

Similar expressions hold for $\vec{K} \cdot \Delta\vec{K}$.

APPENDIX D: APPLICABILITY OF WIGNER-ECKART THEOREM

In the usual formulation of perturbation theory, in which the perturbation operator transforms as a basis function for an irreducible representation of the symmetry group, there is an established procedure for determining how degeneracies are removed by the perturbation. Application of the Wigner-Eckart theorem¹⁶ yields information as to the number of split-off levels and the ratios of the splittings. In the present formulation both the crystalline potential and the expansion functions are changed by the strain. The operators and eigenfunctions are first expressed in a representation which depends on the state of strain. In this representation the Schrödinger equation is expressed as the matrix eigenvalue equation

$$\underline{H}\vec{c} = E\underline{S}\vec{c} , \quad (D1)$$

which, in a truncated representation, is finite dimensional. The "operators" (i.e., matrices) \underline{H} and \underline{S} for the strained crystal can be written as

$$\underline{H} = \underline{H}^0 + \underline{\Delta H} , \quad (D2a)$$

$$\underline{S} = \underline{S}^0 + \underline{\Delta S} , \quad (D2b)$$

where \underline{H}^0 and \underline{S}^0 apply to the unstrained crystal and $\underline{\Delta H}$, $\underline{\Delta S}$ are proportional to the strain. To establish the applicability of the Wigner-Eckart theorem one first has to examine what is meant by the transformation properties of \underline{H} , \underline{S} , and the eigenfunctions \vec{c}^n under point operations (proper and improper ro-

tations).

The set of basis functions for the representation chosen consists of unsymmetrized plane waves, all having the same reduced wave vector \vec{k} , as well as Bloch sums of ALF's with the same wave vector. In addition to these functions the set includes similar functions with wave vectors corresponding to the remaining members of the "star of \vec{k} " in the unstrained crystal.²⁴ The basis functions for the unstrained crystal clearly transform into one another under the point operations of the cubic group O_h . It is thus possible to express an arbitrary operator, P_R of O_h , in this representation; this is designated as the matrix \underline{P}_R . Designating an arbitrary basis function as $\phi_i(\vec{r})$, one finds

$$P_R \phi_i = \sum_j \phi_j [P_R]_{ji} , \quad (D3)$$

where $[P_R]_{ji}$ is the j , i th element of the matrix \underline{P}_R . In this representation "wave functions" (i.e., column vectors) transform according to the rule

$$\vec{c} \rightarrow \underline{P}_R \vec{c} , \quad (D4a)$$

while "operators" (i.e., matrices) transform like

$$\underline{Q} \rightarrow \underline{P}_R \underline{Q} \underline{P}_R^{-1} . \quad (D4b)$$

The operators \underline{H}^0 and \underline{S}^0 are clearly invariant under the operations of the cubic group, whereas the operators \underline{H} , \underline{S} , $\underline{\Delta H}$, and $\underline{\Delta S}$ are invariant under the subgroup of point operations corresponding to the tetragonal (trigonal) group. To examine how these latter operators transform under O_h , one first takes positive strain as corresponding to elongation of the crystal along z with contraction along x and y sufficient to conserve volume (tetragonal case). One then imagines a similar strain in which the x axis is unique, and a third strain in which the y axis is unique. Since the perturbation is linear in the strain and since the operations of O_h merely permute x , y , and z with possible sign changes, the set of three operators above must transform among themselves under the operations of O_h . Moreover, since the superposition of equal strain parameters for each of x , y , and z corresponds to zero strain (due to the volume-preservation condition), one can easily deduce that the three strains correspond to a two-dimensional irreducible representation of O_h (i.e., only two of the three strains are independent). One then readily deduces that the operators $\underline{\Delta H}$ and $\underline{\Delta S}$ transform as the basis function $2z^2 - x^2 - y^2$ of Γ_{12} of O_h . For the trigonal case similar arguments show that $\underline{\Delta H}$ and $\underline{\Delta S}$ transform like $yz + xz + xy$, the sum of the three (standard) basis functions of Γ_{25} of O_h .

In Dirac notation the perturbation theoretic result is, to first order,²⁵

$$\Delta E_n = \langle \vec{c}^{0,n} | \underline{\Delta H} - E_n^0 \underline{\Delta S} | \vec{c}^{0,n} \rangle . \quad (D5)$$

The $\vec{c}^{0,n}$ are eigenvectors of the unperturbed Hamiltonian; those which are degenerate with one another will be different partners of a given irreducible representation of O_h . Since the

operator in Eq. (D5) is also a basis function for a representation of O_h , all the conditions for the applicability of the Wigner-Eckart theorem are fulfilled.

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¹D. Gray and E. Brown, Phys. Rev. **160**, 567 (1967).

²For cubic crystals an arbitrary strain can be expressed as a linear combination of these three strains.

³M. I. Chodorow, Ph. D. thesis (MIT, 1939) (unpublished).

⁴H. L. Davis, J. S. Faulkner, and H. W. Joy, Phys. Rev. **167**, 601 (1968).

⁵E. Brown and J. A. Krumhansl, Phys. Rev. **109**, 30 (1958).

⁶A. Marcus, Phys. Rev. **135A**, 527 (1964).

⁷D. Gray and A. Marcus Gray, Bull. Am. Phys. Soc. **16**, 314 (1971); Watervliet Arsenal Technical Report No. 7216, 1972 (unpublished).

⁸G. E. Juras and B. Segall, Phys. Rev. Lett. **29**, 1246 (1972).

⁹G. E. Juras and B. Segall, Surf. Sci. **37**, 929 (1973).

¹⁰Equation (7) is similar to the usual second-order perturbation expression with $|H'_{mm}|$ replaced by ΔE_A , due to the presence of the S matrix. In deriving Eq. (7) only those second-order terms were kept which contained $(E_n^0 - E_m^0)$ in the denominator.

¹¹Charles Kittel, *Introduction to Solid State Physics*, 2nd ed. (Wiley, New York, 1956).

¹²The E^0 levels for the same representation also differ slightly in Tables I-IV, due to the use of slightly different maximum $|\vec{k} + \vec{K}|$ values in the plane-wave expansion. In general, the E^0 values in Tables II-IV are higher than the corresponding Table I values, since in the lower symmetry more plane waves are required to reach the same $|\vec{k} + \vec{K}|$ value; in many cases computer time and storage considerations precluded use of such a large number of plane waves.

¹³G. A. Burdick, Phys. Rev. **129**, 138 (1963).

¹⁴Because these ratios are predicted by symmetry it is really sufficient to compute just *one* of the paired values; all values were actually evaluated in order to have a check on the numerical computation. To obtain good agreement with the predicted ratios in an MPW formula-

tion, the sets of expansion functions in the cases being compared must "match"; i.e., if a plane wave of a given $|\vec{k} + \vec{K}|$ is used in one of the representations, all plane waves of the same $|\vec{k} + \vec{K}|$ that are allowed by symmetry must be included in the representation being compared.

¹⁵In the present calculation a slightly different potential was used to prevent overlap of potentials in the muffin-tin spheres under compression.

¹⁶B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill, New York, 1963), pp. 39-41.

¹⁷The theorem is also valid for $|\psi_{\alpha,j}\rangle$ replaced by $|\psi_{\beta,j}\rangle$; the restriction to " α - α " integrals is made here since, in determining *ratios*, the present paper is not concerned with mixing between different fcc levels.

¹⁸Juras and Segall (Refs. 8 and 9) have an error in their assignment of this second-order shift; the mixing with X_2 can only affect *one* of the two originally degenerate X_5 levels.

¹⁹G. F. Koster, Solid State Phys. **5**, 174 (1957).

²⁰When the fcc real-space structure is stretched in the z direction, the Brillouin zone begins to look like Fig. 9(b) of Ref. 19.

²¹R. H. Parmenter, Phys. Rev. **100**, 573 (1955).

²²L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).

²³When the fcc real-space structure is stretched along the [111] axis, the Brillouin zone begins to look like Fig. 16(b) of Ref. 19.

²⁴This basis set consists of many more functions than are actually used in the numerical calculations. The numerical calculations utilize symmetrization procedures from group theory in order to reduce the size of the matrices. However, neither the numerical eigenvalues nor the conclusions reached here are affected by this procedure.

²⁵This is Eq. (3) of the main text.