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Selection Rules for Point-Defect Anelastic Relaxations: Classical *versus* Quantum Mechanical*

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Abstract. A quantum mechanical analysis of selection rules for point-defect relaxations under an applied stress yields different results than a conventional classical analysis. The difference in the two approaches is illustrated using a simple 4-well model. The classical selection rules are a special case of the quantum mechanical selection rules with the wavefunctions of the reorienting defect atoms highly localized in potential minima, such that off-diagonal matrix elements of the stress perturbation are negligible.

1. INTRODUCTION

Selection rules for anelastic relaxations of point defects in crystals can be derived either classically [1-5] or quantum mechanically [6]. Almost all studies use classical selection rules. The relatively few studies that treat anelastic relaxations from a fully quantum mechanical perspective focus on point defects in semiconductors where classical descriptions of the defect states are clearly inadequate (see, for example, Refs. 7-9). The results of the classical and quantum mechanical approaches differ for some defect symmetries. As described in this report, these differences arise from the inability of classical analyses to consider the finite spatial extent of wavefunctions and the resulting neglect of off-diagonal matrix elements of the stress perturbation.

2. CLASSICAL SELECTION RULES

Perhaps the simplest model for illustrating the difference between classical and quantum mechanical selection rules is an atom in a tetragonal 4-well potential. Consider an impurity atom A at a tetragonal (D_{4h}) site in a crystal lattice (e.g., centered between next-nearest neighbors in a BCC lattice) and a second atom B trapped near atom A in the plane with four-fold rotational symmetry, as shown in Fig. 1. Atom A is considered to be immobile at the temperatures of interest. Classically, atom B is localized in one of four equivalent potential wells (a , b , c or d) indicated by dashed circles in Fig. 1 and can be thermally excited from one well to another.

If the crystal lattice is elastically distorted by external stress, the four potential minima may become nonequivalent, depending on the symmetry of the distortion. Two types of pure-shear elastic strain (Fig. 2) are considered here. One, ϵ_2 , consists of an extension along $\hat{x}$ and a compression along $\hat{y}$, such that the unit cell does not change volume. The other, ϵ_3 , consists of an extension along $\hat{x}+\hat{y}$ and a compression along $\hat{x}-\hat{y}$ with no change in volume.

The classical selection rules of the defect under ϵ_2 and ϵ_3 can be determined by inspection of Figs. 1 and 2. Under ϵ_2 , the four potential minima of atom B remain energetically equivalent. Under ϵ_3 , minima a and c become different than b and d , so that an ensemble of similar defects in a crystal undergoes a thermally activated repopulation between the potential minima, and a corresponding anelastic strain relaxation occurs.

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Figure 1: Model defect with atom A at a D_{4h} site and, classically, atom B (not shown) localized in one of the wells a , b , c , or d .

Figure 2: Shear strains.

3. QUANTUM MECHANICAL SELECTION RULES

Viewed from a quantum mechanical perspective, the states of atom B could have wavefunctions ϕ_a , ϕ_b , ϕ_c , and ϕ_d highly localized in the four potential wells a , b , c , and d , respectively, so that a classical derivation of the selection rules would be valid. If this were the case, the four wavefunctions would be orthogonal because of their lack of overlap, but not because of their symmetry. The fact that such states are not orthogonal on the basis of symmetry can be immediately deduced from the group-theoretical character table of D_{4h} (Table A.1 in the Appendix), which shows the highest degeneracy to be two-fold.

Table 1: Character table for $\phi_a - \phi_d$. Definitions of the symmetry operations are given in the Appendix.

	E	C_{2x}	C_{2y}	C_{2z}	C_{4z}	C_{4z}^{-1}	$C_{2\alpha}$	$C_{2\beta}$	I	IC_{2x}	IC_{2y}	IC_{2z}	IC_{4z}	IC_{4z}^{-1}	$IC_{2\alpha}$	$IC_{2\beta}$
Γ	4	0	0	0	0	2	0	0	0	0	4	0	0	0	2	2

The characters of the reducible representation Γ formed by $\{\phi_a \dots \phi_d\}$ are given in Table 1. This representation reduces to $\Gamma^1 \oplus \Gamma^3 \oplus \Gamma^{10}$ with symmetrized basis wavefunctions given in terms of $\phi_a - \phi_d$ by

$$\psi^1 = 4^{-1/2}[\phi_a + \phi_b + \phi_c + \phi_d] \quad (1)$$

$$\psi^3 = 4^{-1/2}[\phi_a - \phi_b + \phi_c - \phi_d] \quad (2)$$

$$\psi_1^{10} = 4^{-1/2}[\phi_a - \phi_b - \phi_c + \phi_d] \quad (3)$$

$$\psi_2^{10} = 4^{-1/2}[\phi_a + \phi_b - \phi_c - \phi_d], \quad (4)$$

where the superscripts indicate the irreducible representations to which the wavefunctions belong. With negligible overlap of $\{\phi_a \dots \phi_d\}$, the four symmetrized states have the same energy in the undistorted lattice. However, with finite overlap, ψ^1 and ψ^3 are nondegenerate (barring further accidental degeneracies), and ψ_1^{10} and ψ_2^{10} are degenerate. Therefore, if $\{\phi_a \dots \phi_d\}$ are allowed to overlap, the energy level of ψ_1^{10} and ψ_2^{10} is the only one that can be split by an applied stress. Because of this, ψ_1^{10} and ψ_2^{10} are the focus here in considering selection rules.

Quantum mechanical selection rules for the model defect can be determined from group theory alone. A brief summary of the group theoretical analysis is presented in the Appendix. The strains ϵ_2 and ϵ_3 introduce perturbations to the Hamiltonian for atom B, H'_2 and H'_3 , that transform according to Γ^2 and Γ^3 , respectively. With both of these perturbations, the degeneracy of ψ_1^{10} and ψ_2^{10} is removed. Therefore, the quantum mechanical selection rules disagree with the classical selection rules with respect to the effect of ϵ_2 . The quantum analysis indicates that ϵ_2 can split the energy levels; the classical analysis forbids this splitting.

The source of this difference can be understood by considering the perturbing Hamiltonian in the $\{\phi_a \dots \phi_d\}$ basis. With no overlap, the diagonal matrix elements of H'_2 correspond to the classical shifts in energy of the four states (the same for all four states), and the off-diagonal matrix elements are zero:

$$H'_2 \sim \epsilon_o \begin{pmatrix} U & 0 & 0 & 0 \\ 0 & U & 0 & 0 \\ 0 & 0 & U & 0 \\ 0 & 0 & 0 & U \end{pmatrix} \quad (5)$$

where ϵ_o is the magnitude of the strain and U is a constant. If this were the exact perturbation, ψ_1^{10} and ψ_2^{10} would not be split.

If $\{\phi_a \dots \phi_d\}$ are allowed to have finite overlap between adjacent potential wells, some of the off-diagonal matrix elements will be nonzero. From an inspection of Figs. 1 and 2 and a consideration of the symmetries with respect to the reversal of the sign of the strain, the perturbation in the $\{\phi_a \dots \phi_d\}$ basis is found to be

$$H'_2 \sim \epsilon_o \begin{pmatrix} V & W & 0 & -W \\ W & V & -W & 0 \\ 0 & -W & V & W \\ -W & 0 & W & V \end{pmatrix} \quad (6)$$

where V and W are constants and W is assumed to be real. The matrix elements between ψ_1^{10} and ψ_2^{10} are

$$\langle \psi_1^{10} | H'_2 | \psi_1^{10} \rangle = \epsilon_o(V - 2W) \quad (7)$$

$$\langle \psi_2^{10} | H'_2 | \psi_2^{10} \rangle = \epsilon_o(V + 2W) \quad (8)$$

$$\langle \psi_1^{10} | H'_2 | \psi_2^{10} \rangle = 0 \quad (9)$$

$$\langle \psi_2^{10} | H'_2 | \psi_1^{10} \rangle = 0. \quad (10)$$

The degeneracy of ψ_1^{10} and ψ_2^{10} is removed by ϵ_2 . The difference between this result and the classical result arises from the neglect of off-diagonal matrix elements (W) in the classical model.

Even though ϵ_2 is found to produce anelastic relaxation on the basis of pure symmetry arguments, this relaxation may be negligible compared to that produced by ϵ_3 . An analysis of the relative significance of the off-diagonal matrix elements is beyond the scope of this paper. One qualitative feature that should be noted is that the rate of quantum tunneling between adjacent potential minima decreases rapidly with increasing barrier height and increasing mass of the tunneling atom. Therefore, classical selection rules will be valid for relaxations involving activation energies and defect masses that are sufficiently large.

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Appendix

The character table for D_{4h} is given in Table A.1. The notation used for the representations and symmetry operations follows that given by Cornwell [10], except that the symbols α and β are used for the diagonal symmetry axes (Fig. 1) that Cornwell denotes by a and b . E is the identity operation. I is the inversion operation. C_{2x} , C_{2y} , $C_{2\alpha}$, and $C_{2\beta}$ are two-fold rotations about the x , y , α , and β axes, respectively. C_{2z} and C_{4z} are two-fold and four-fold rotations about the axis perpendicular to the plane of Fig. 1.

Table A.1: Character table for D_{4h} .

		E	C_{2x} C_{2y}	C_{2z}	C_{4z} C_{4z}^{-1}	$C_{2\alpha}$ $C_{2\beta}$	I	IC_{2x} IC_{2y}	IC_{2z}	IC_{4z} IC_{4z}^{-1}	$IC_{2\alpha}$ $IC_{2\beta}$
Γ^1	A_{1g}	1	1	1	1	1	1	1	1	1	1
Γ^2	B_{1g}	1	1	1	-1	-1	1	1	1	-1	-1
Γ^3	B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
Γ^4	A_{2g}	1	-1	1	1	-1	1	-1	1	1	-1
Γ^5	E_g	2	0	-2	0	0	2	0	-2	0	0
Γ^6	A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
Γ^7	B_{1u}	1	1	1	-1	-1	-1	-1	-1	1	1
Γ^8	B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
Γ^9	A_{2u}	1	-1	1	1	-1	-1	1	-1	-1	1
Γ^{10}	E_u	2	0	-2	0	0	-2	0	2	0	0

Table A.2: Notations of Cornwell [10] and Koster *et al.* [11] for the irreducible representations of D_{4h} .

Cornwell	Γ^1	Γ^2	Γ^3	Γ^4	Γ^5	Γ^6	Γ^7	Γ^8	Γ^9	Γ^{10}
Koster <i>et al.</i>	Γ_1^+	Γ_3^+	Γ_4^+	Γ_2^+	Γ_5^+	Γ_1^-	Γ_3^-	Γ_4^-	Γ_2^-	Γ_5^-

The tables of coupling coefficients presented by Koster *et al.* [11] are used to determine selection rules. Unfortunately, the numbering used by Koster *et al.* for the irreducible representations of D_{4h} does not match that of Cornwell [10]. Table A.2 gives the translation between the notations of these two references. A detailed description of the use of the tables of Koster *et al.* is beyond the scope of this paper. However, for the symmetries of the states and strains of interest here, the procedure is relatively simple. The perturbations H'_2 and H'_3 in the $\{\psi_1^{10}, \psi_2^{10}\}$ basis have the same form as the corresponding matrices of coupling coefficients within a similarity transformation and a multiplicative constant. In the diagonalized $\{\psi_1^{10}, \psi_2^{10}\}$ basis, the perturbation from ϵ_2 is found to have matrix elements C_2 and $-C_2$, where C_2 is a constant. This is the same result as that presented in Eqs. (7)-(10), except that the group theoretical analysis provides the additional information that V must be 0. Similarly, the diagonalized perturbation from ϵ_3 has matrix elements C_3 and $-C_3$, where C_3 is a second constant. Classical selection rules will be valid if C_2 is much less than C_3 .

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