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USING SYMMETRY IN FROZEN PHONON CALCULATIONS

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Software has been developed which applies group-theoretical methods to the calculation of phonon spectra. The software draws on a large data base which includes information on each of the 230 crystallographic space groups and their irreducible representations. The software finds the optimal phonon modes for the frozen-phonon energy calculations.

Keywords: Phonon, symmetry

Over the past ten years, Stokes and Hatch[1–4] have been developing software for applying group-theoretical methods to phase transitions in crystalline solids. This software package, named ISOTROPY, uses a large data base which includes information about the 230 crystallographic space groups (symmetry elements, Wyckoff positions, etc.), their irreducible representations, and isotropy subgroups. ISOTROPY allows us access to this data base, selecting the information desired and displaying it in an organized manner. ISOTROPY also does additional calculations, such as finding invariant polynomials in the expansion of the Landau free energy and projecting distortion modes in a phase transition. (ISOTROPY is now available for installation upon request.[5])

As an example of how ISOTROPY can be useful in many different areas of research in solid state physics, we discuss in this paper its application to frozen phonon calculations. These calculations provide information about normal modes of oscillation in a crystal.

In this method, the possible atomic displacements in a crystal are organized into collective modes (not necessarily the normal modes),

$$\psi_i = \{\Delta \mathbf{r}_{ij}\}. \tag{1}$$

In the ith mode ψ_i, the jth atom is displaced by an amount $\Delta \mathbf{r}_{ij}$. A general distortion in the crystal can be written as

$$\psi = \sum_i C_i \psi_i. \tag{2}$$

For such a distortion, the total potential energy of the crystal can be written in the form,

$$E = E_0 + \frac{1}{2} \sum_{ij} A_{ij} C_i C_j \tag{3}$$

(using the harmonic approximation). The normal modes and their frequencies ω are obtained by solving the coupled equations,

$$m_i\omega^2 C_i = \sum_j A_{ij} C_j, \tag{4}$$

where m_i is the mass of the atoms in the ith mode. (Each mode contains displacements for one kind of atom only.) If the modes are correctly chosen, the matrix A will be in block-diagonal form, allowing us to solve Equation (4) for one block at a time.

The matrix elements of A are obtained by calculating the energy of various frozen phonons. In an n-dimensional block, there are $\frac{1}{2}n(n+1)$ elements of A to be determined (A is symmetric). To obtain these elements, the energy of $\frac{1}{2}n(n+1)$ different frozen phonons must be calculated. Therefore, it is advantageous to choose the modes so that the blocks along the diagonal of A are as small as possible.

Using group-theoretical methods, we can easily make this optimal choice. We simply construct modes which transform like basis functions of the irreducible representations (IR's) of the crystal's space group G. The modes which transform like the same basis function of the same IR belong to the same block along the diagonal of A.

As an example, consider the crystal $CaCuO_2$. Its space-group symmetry is $P4/mmm$ (tetragonal). The structure of $CaCuO_2$ is shown in Figure 1. In this example, we consider the M point which is at $\mathbf{k} = (\pi/a, \pi/a, 0)$. There are 10 IR's of $P4/mmm$ belonging to M. Using one IR at a time, we project out modes which transform like basis functions of that IR.[3] The results are shown in Table I. The labeling of IR's follows the convention of Miller and Love.[6] (Note that there are no modes which transform like basis functions of M_1^- or M_4^-.)

The number of blocks in A resulting from modes belonging to a particular IR is equal to the dimension of that IR. Each block contains modes which transform like one of the basis functions of the IR. (An n-dimensional IR has n basis functions.) Furthermore, each block is identical. This gives rise to n-fold degenerate normal modes. All of the IR's except M_5^+ and M_5^- are one-dimensional. Their normal modes are nondegenerate. IR's M_5^+ and M_5^- are two-dimensional. Their normal modes are two-fold degenerate.

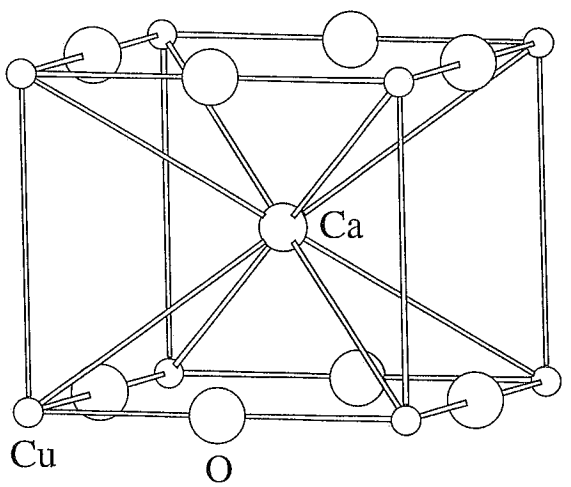

FIGURE 1 The unit cell of $CaCuO_2$.

TABLE I

Projected modes at the M point for $CaCuO_2$. In the columns are given the irreducible representation, the atoms displaced in the modes, the number and dimension of blocks along the diagonal of matrix A, and the space-group symmetry of the resulting frozen phonons.

IR	Atoms	Blocks		Symmetry
		#	Dim	
M_1^+	O	1	1	$P4/mmm$
M_2^+	O	1	1	$P4/mbm$
M_3^+	O	1	1	$P4/mbm$
M_4^+	O	1	1	$P4/mmm$
M_5^+	O	2	1	$Pmna, Cmma, P2/c$
M_2^-	Ca	1	1	$P4/nmm$
M_3^-	Cu	1	1	$P4/nmm$
M_5^-	Ca,Cu	2	2	$Pmma, Cmmm, P2/m$

The dimension of each block in A is equal to the number of different modes which can be constructed to transform like one of the basis functions of the IR. All of the IR's except M_5^- can project out only one mode for each of its basis functions. Each mode involves the displacements of only one kind of atom. M_5^+ is two-dimensional and thus projects out two modes, one for each of its basis functions. These two modes belong to two identical one-dimensional blocks in A.

M_5^- projects out two modes for each of its basis functions. One mode involves displacements of Ca and the other involves displacements of Cu. Since M_5^- is two-dimensional, there are four modes all together, two in each of the two identical blocks in A.

To obtain all of the normal modes at the M point, we solve Equation (4) for seven one-dimensional blocks and one two-dimensional block.

The frozen phonon associated with each mode generally reduces the symmetry of the crystal. The space group of the distorted crystal is an *isotropy subgroup* of G. In Table I, we list the isotropy subgroups for each of the IR's.[4] For one-dimensional IR's, there is only one isotropy subgroup, since there is no freedom of choice in the distortion.

M_5^+ and M_5^- are two-dimensional, and we see that more than one isotropy subgroup are listed for these IR's. Consider M_5^-. For this IR, there are two identical blocks in A. This means that the modes in those two blocks may be mixed without changing the elements in the blocks. Let ψ_{ij} be the jth block. We form new modes in the following way:

$$\phi_j = \sum_i \eta_i \psi_{ij}, \tag{5}$$

where the coefficients η_i are independent of j. They constitute a vector $\boldsymbol{\eta} = (\eta_1, \eta_2)$ in representation space. In phase transition theory, $\boldsymbol{\eta}$ is called the *order pa-*

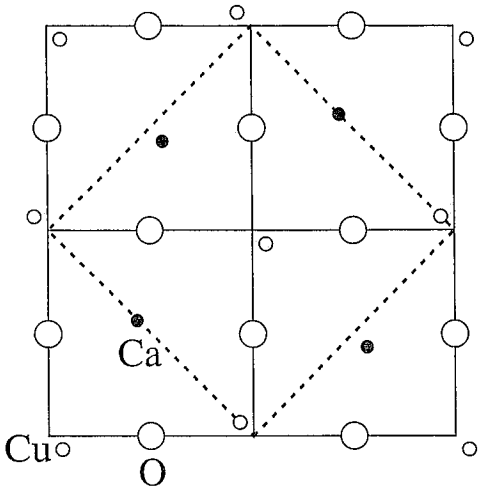

FIGURE 2 Frozen phonon in $CaCuO_2$ for IR M_5^- and $\boldsymbol{\eta} = (a, 0)$. The space-group symmetry is *Pmma*. The figure shows the projection of the crystal onto the *xy* plane. The unit cells of *P4/mmm* are indicated by the solid lines. The unit cell of *Pmma* is indicated by the dashed line. The Cu's and Ca's are displaced in the $\pm(\mathbf{a} - \mathbf{b})$ directions.

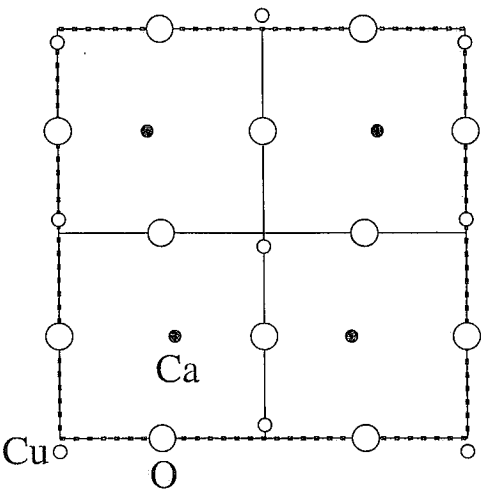

FIGURE 3 Frozen phonon in $CaCuO_2$ for IR M_5^- and $\boldsymbol{\eta} = (a, a)$. The space-group symmetry is *Cmmm*. The figure shows the projection of the crystal onto the *xy* plane. The unit cells of *P4/mmm* are indicated by the solid lines. The unit cell of *Cmmm* is indicated by the dashed line. The Cu's are displaced in the $\pm\mathbf{b}$ directions and the Ca's are displaced in the $\pm\mathbf{a}$ directions.

rameter. These two new distortions, ϕ_1 and ϕ_2, form a block in A with the same elements as the blocks for ψ_{ij}. The choice of $\boldsymbol{\eta}$ does not affect the elements in the block, but it does affect the symmetry of the frozen phonon. For the choice of IR matrices used in ISOTROPY, $\boldsymbol{\eta} = (a, 0)$ and $\boldsymbol{\eta} = (0, a)$ result in the isotropy subgroup *Pmma*, $\boldsymbol{\eta} = (a, \pm a)$ results in the isotropy subgroup *Cmmm*, and any other choice of $\boldsymbol{\eta}$ results in the isotropy subgroup *P2/m*.[4] The frozen phonons for $\boldsymbol{\eta} = (a, 0)$ and $\boldsymbol{\eta} = (a, a)$ are shown in Figures 2 and 3, respectively. Note that the two phonons represented by the two figures have the same frequency. They represent degenerate modes.

Sometimes, the symmetry of a frozen phonon can greatly affect the efficiency of an energy calculation. In that case, we choose the $\boldsymbol{\eta}$ that results in the optimal symmetry of the isotropy subgroup. For example, sometimes the size of the unit

cell is different for different isotropy subgroups. This can occur when there are more than one **k** vector ("arm") in the star of **k**. Subgroups with larger unit cells satisfy $\mathbf{k}\cdot\mathbf{R} = 2\pi n$ simultaneously for more than one **k** (arm) in the star. We generally want to choose the isotropy subgroup with the smallest unit cell.

The situation becomes more complicated for complex IR's. The matrices of these IR's contain complex elements. We avoid complex numbers in our calculations by forming a *physically* irreducible representation (PIR). This is done by forming the direct sum of each IR matrix with its complex conjugate. An appropriate transformation can then bring the matrices to real form. These matrices are irreducible with respect to real numbers. However, since they are not true IR's, they do not automatically produce a separate block in A for each dimension of the PIR. (This problem is caused by the failure of the orthogonality theorem for PIR's).

The solution to this dilemma is presented here without proof.[7] If we choose modes which have the symmetry of one of the isotropy subgroups for the PIR, they will form a block in A. As an example, let us consider a rather complicated case. The IR W_1 of space group $Fm\bar{3}c$ is six-dimensional and complex. We form the twelve-dimensional PIR W_1W_2. (The IR W_2 happens to be the complex conjugate of W_1.) There are 26 different isotropy subgroups for this PIR.[4] The cell sizes for these subgroups range from 4 to 32 times the cell size of the undistorted crystal. We choose one of the subgroups ($I\bar{4}m2$) with the smallest possible cell size ($4\times$). We find that the order parameter for this subgroup is $\boldsymbol{\eta} = (a, 0, 0, 0, 0, 0, b, 0, 0, 0, 0, 0)$. The two numbers, a and b, are arbitrary. This means that modes which transform like the 1st basis function of the PIR produce the symmetry of $I\bar{4}m2$, and modes which transform like the 7th basis function produce the symmetry of $I\bar{4}m2$. Any combination of the two modes will also produce the symmetry of $I\bar{4}m2$. Since we do not know which combinations belong in different blocks [and in fact cannot know until after the solution of Equation (4)], we must include both kinds of modes. The block will contain modes that transform like the 1st basis function of W_1W_2 and modes that transform like the 7th basis function of W_1W_2. The dimension of the block will be twice the number of modes projected out for each basis function of the PIR.

In this example, the order parameter has two degrees of freedom. It can be shown that for a PIR formed from a complex IR, all order parameters must have at least two degrees of freedom. Therefore, the block formed in this example is the smallest possible, using symmetry arguments alone.

ISOTROPY makes all of these calculations simple to perform. It lists for any IR or PIR the isotropy subgroups along with related information, such as the size of the unit cell and the vectors of the primitive lattice. ISOTROPY also projects out modes and lists the atomic displacements which have the symmetry of any chosen isotropy subgroup. These modes can then be used in frozen-phonon energy calculations to obtain the elements in the block on the diagonal of matrix A. These are powerful techniques for using symmetry and are very simple to apply using ISOTROPY.

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