Group Theory Applied to Nonlinear Phononics

Kelson Kaj[1]

[1]*Department of Physics, University of California at San Diego, La Jolla, CA 92093*

With the ability to create high-field THz and mid-IR ultrafast pulses, physicists have been able to directly drive phonons to large enough amplitudes where anharmonicities and nonlinear phonon couplings become highly relevant for the induced dynamics. This new field has been dubbed "nonlinear phononics," and these ideas have been used to drive materials to previously inaccessible structural, magnetic, and electronic phases. Here the relevance and constraints due to group theory will be explained for this new field of ultrafast experiments.

INTRODUCTION

The ability to drive solids to new phases with ultrashort pulses has created a new field of photo-induced phase transitions in roughly the past two decades. Light can be used to access the many different degrees of freedom of solids: charge, spin, orbital, and lattice. The high intensity light required of some of these excitations is easier to generate for visible and NIR wavelengths, and many early studies used this kind of light as an intense pump [1, 2]. Access to driving of phonons was mostly limited to indirect coupling between electronic and lattice degrees of freedom, as most phonons lie in mid-IR or far-IR wavelength ranges.

However, in recent years the ability to generate more intense THz and mid-IR pulses gives the ability to drive lower energy degrees of freedom, like phonons, directly to large amplitudes. The strong relationship between crystal structure and electronic or magnetic phases means that driving phonons can and has been shown experimentally to access either new phases of matter for materials, or phases at very different temperatures than the equilibrium phase diagram [3]. A key necessity both for access and stabilization of these phases is the ability to excite not only IR-active phonons, which can be directly driven with light pulses, but also Raman-active phonons. Due to nonlinear phonon coupling between different phonons, which become relevant as IR active phonons are driven to large amplitudes, Raman modes can not only be driven to oscillate at large amplitudes, but also around new minima at displaced coordinates [4]. In this paper I will first describe crystal symmetries, their representations, and phonons. Then I will apply these concepts to nonlinear phonon couplings, and discuss constraints and qualitatively different behaviors for nonlinear phononics that arise due to group theory and symmetries of different crystals.

CRYSTAL SYMMETRIES

All crystals (excluding quasicrystals) have symmetry that is given by their space group. The space group is made up of combining the point groups with translation operations, there are 230 in total [5]. Crystallographic point groups are made up of the symmetry operations that leave a crystals unit cell unchanged, but with the restriction that for crystals the demand of translational symmetry restricts the rotational symmetry to be 1, 2, 3, 4 or 6-fold [5]. The symmetry operations that are involved in space groups are the following: the idenity, rotations, reflections, inversions, and improper rotations (which are a combination of a rotation and a reflection) [5].

There are many space groups and they have intimidating names, but since crystal databases use these names it would be good to understand a bit of what they mean. In international notation, space groups will have names of the form Abbb, for example Pmm2. The first uppercase letter corresponds to the type of Bravais Lattice the crystal is made up of, in this case the P is for primitive. The following elements then describe the symmetry operations for the x, y, and z axes, the m corresponds to a mirror plane, while the 2 corresponds to 2-fold rotational symmetry. If all axes had 2-fold rotational symmetry the group would be P222, while if an axis has both a mirror plane and an n-fold rotation axis, these are written together as a fraction, for example $P\frac{4}{m}\frac{2}{m}\frac{2}{m}$ [6].

REPRESENTATIONS AND PHONONS

The coordinates of the ions in a lattice live in a dN representation of the symmetry group for the crystal, d being the number of spatial dimensions and N the number of ions [7]. These representations also have their own dictionary that is good to have some idea of even if the names feel arbitrary or misplaced. These representations have names like A_{1g}, B_{2u}, or E_{2u}. The A means the representation is symmetric with respect to rotation about the principle axis, while B or E mean it is antisymmetric with respect to rotations about the principle axis, B being for 1d representations and E for 2d representations. The subscript number represents whether the representation is symmetric (1) or antisymmetric (2) with respect to reflection about the plane perpendicular to the principle axis, while the subscript letter corresponds to being symmetric (g) or antisymmetric (u) with respect to in-

version [6].

An important distinction for physics in general and for nonlinear phononics is the difference between IR and Raman active phonons. Physically, for a phonon to be IR active it needs to involve a change in the dipole moment for a molecule, while for a phonon to be Raman active it needs to involve a change in the polarizability of a molecule [6]. From a group theory perspective, the difference between IR and Raman active has to do with how the symmetry operations for a given representation compare with given mathematical functions. The mathematical functions for IR and Raman modes are a fairly common addition to character tables in chemistry, an example is shown below. For IR-active modes, the representation must transform like the linear functions x, y, or z, while Raman-active modes transform like products, $x^2, yz, x^2 + y^2, etc.$ [8].

FIG. 1: From [8], showing character table for point group C_{2v} including columns with mathematical functions that transform with given symmetry

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

For multiplying representations together, the overall rules are somewhat as expected, symm ⊗ symm =symm, anti ⊗ anti=symm, anti ⊗ symm=anti, for both A and B and the subscripts(i.e. $A \otimes A = A, A \otimes B = B, A \otimes B = B$). This really is all there is to it for the 1-d irreps, but when higher dimensional representations are multiplied (E and T), the products are obtained by looking for the breakdown of irreps the new reducible representation is made up of. This can be accomplished with the character table, and the number of irreps contained in a reducible representation is given by the following formula [8]:

$$n_\alpha = \frac{1}{|G|} \sum_h \chi_{red} \chi_\alpha g(h) \qquad (1)$$

Here α is a label of a given irrep., $|G|$ is the order of the group, χ refers to a character for the reducible or irreducible representation, and g(h) is the number of elements for the given conjugacy class h, all of which come from the character table for a given group. Products of more than two higher-dimensional irreps can be decomposed the same way.

APPLICATIONS TO NONLINEAR PHONONICS

Nonlinear phononics involves looking at the potential energy of the lattice, including terms beyond the quadratic harmonic oscillator terms. Here is an example for general phonons that are simply labelled as being IR and Raman active (using the same conventions as [4]:

$$V = \frac{1}{2}\Omega_R^2 Q_R^2 + \frac{1}{2}\Omega_{IR}^2 Q_{IR}^2 + \frac{1}{3}a_3 Q_R^3 + \frac{1}{4}b_4^2 Q_{IR}^4 - \frac{1}{2}gQ_R Q_{IR}^2 \qquad (2)$$

As mentioned previously, the idea of nonlinear phononics is generally to be able to drive Raman-active modes to large amplitudes, so the important piece of the potential is the coupling terms, above this is $Q_R Q_{IR}^2$. To know which terms are allowed, we need to look at the representations involved in the multiplication of the above term. The allowed terms must contain (though don't need to solely contain) the totally symmetric A_g representation [4].

Depending on the type of mode one wants to couple to, qualitatively different behavior can occur. The work by Subedi et. al. explores some of these calculations by looking at $PrMnO_3$ (PMO), with space group Pmna, and La_2CuO_4 (LCO), with space group Bmab [4]. For PMO, which has the point group mmm, each of the irreps. square to the A_g representation. The lowest order possible coupling in this material looks like $Q_R Q_{IR}^2$. For finite amplitudes along the IR coordinate, the minimum in the potential for the Raman coordinate shifts, as can be seen in Fig. 2, taken from [4]. For this case (which can't be derived from simply group theory) driving phonons coupled to these displacements was able to drive an insulator-to-metal transition in PMO [9].

FIG. 2: From [4], showing change to lattice potential energy of Raman-active A_g mode in PMO with cubic coupling
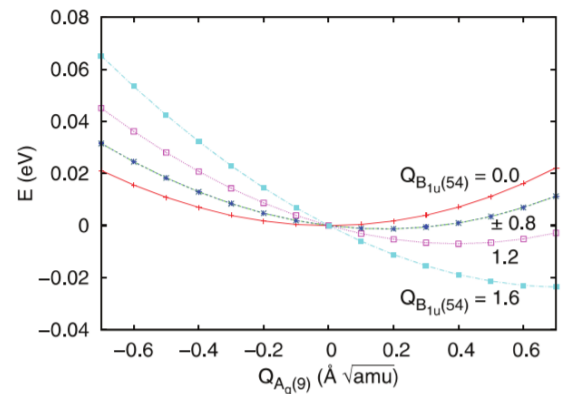
LCO on the other hand does have allowed cubic coupling like in PMO, but the coupling of B-phonons to A_g phonons is small. However, strong coupling does exist between B_{1g} Raman active and B_{3u} IR active modes. However, A_g isn't contained within the product $B_{1g} \otimes B_{3u} \otimes B_{3u}$, so this term doesn't exist, and the lowest coupling term is actually a $B_{1g} \otimes B_{1g} \otimes B_{3u} \otimes B_{3u}$, in other words $Q_R^2 Q_{IR}^2$. This will lead to a qualitatively different potential energy surface, shown in Fig. 3, that involves a double well potential.

Because of the double-well potential, qualitatively different behavior can be acheived for quartic coupling in

FIG. 3: From [4], showing change to lattice potential energy of Raman-active B_{3u} mode in LCO with quartic coupling
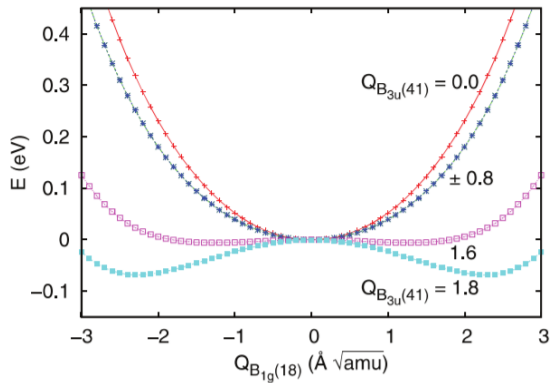
comparison to cubic coupling. For large enough driving, not only can rectification occur (oscillating around a non-zero displacement), but oscillations between the two wells can occur for even larger drives, without any rectification. These different behaviors are illustrated in Fig. 3.

FIG. 4: From [4], showing difference in dynamics of Raman-active B_{3u} phonon for different excitation strengths
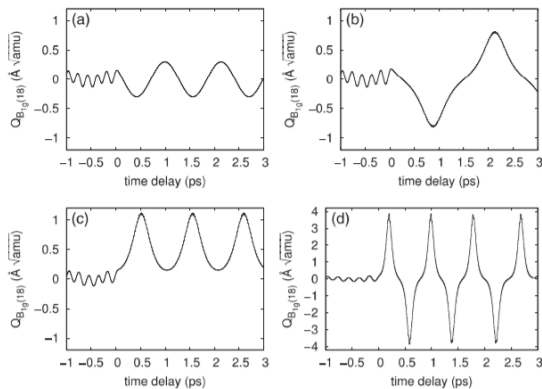
Some time was spent looking through tables of calculated nonlinear phonon coupling constants, of which there is still unfortunately a limited number available as far as what could be found in the literature [3, 4, 10–12]. No nontrivial correlations between characters and nonlinear coupling constants could be found, characters for irreps. are only larger than 1 for higher dimensional E and T modes. That being said, something interesting to note is that in the nonlinear phononics literature, of which there is still a limited amount of work, all of the experiments on crystals that do have E-modes within their irreps have found the strongest coupling between IR and Raman active modes involving and IR-active E-mode [3, 11]. To slighly restate this, the only nonlinear phononics experiments that involve driving an IR-active B-mode have been on crystals whose space group representation does not include any E or T irreps. [3, 4, 10, 12]. Further study to find out why this may be the case could be very interesting. Group theory decides all of the allowed terms in the full lattice potential, and thus the possible types of coupling. However, group theory can't answer why one B_{1g} mode couples to a given A_g mode more than another B_{1g} mode, in order to get the quantitative coupling strengths full DFT calculations need to be done.

CONCLUSION

In this paper I have given a brief introduction to crystal symmetries and their representations for the purpose of understanding the underlying group theory governing nonlinear phononics calculations and experiments. Looking into the symmetry and group theory is the first step that must be taken when designing calculations or experiments, and decides which types of coupling are allowed, but more rigorous quantitative calculations must be done next.

REFERENCES

[1] J Zhang and R. Averitt, "Dynamics and Control in Transition Metal Oxides," Annu. Rev. Mater. Res. 44, 19-43 (2014)

[2] E. Collet et al., "Laser-Induced Ferroelectric Structural Order in an Organic Charge-Transfer Crystal," Science 300(5619), 612–15 (2003)

[3] R. Mankowsky, M. Först, and A. Cavalleri, "Non-equilibrium control of complex solids by nonlinear phononics," Reports on Progress in Physics, 79, 6 (2016)

[4] A. Subedi, A. Cavalleri, and A. Georges, "Theory of nonlinear phononics for coherent light control of solids," Phys. Rev. B 89, 220301 (2014)

[5] N. W. Ashcroft, N. D. Mermin, "Solid State Physics," Harcourt, Orlando, FL (1976)

[6] J. P. Elliott, P. G. Dawber, "Symmetry in Physics," Oxford University Press, New York, 1984

[7] J. McGreevy, "Physics 220: Symmetry in physics Fall 2020," Lecture Notes, UCSD, 2020

[8] B. Nikolic, "Introduction to Solid State Physics," Lecture Notes, U. Delaware, 2005

[9] M. Rini et al., "Control of the electronic phase of a manganite by mode-selective vibrational excitation," Nature, 449, 72-74 (2007)

[10] R. Mankowsky et al. "Nonlinear lattice dynamics as a basis for enhanced superconductivity in YBa2Cu3O6.5," Nature 516 , 71–73 (2014)

[11] A. Disa et al., "Polarizing an antiferromagnet by optical engineering of the crystal field," Nature Physics 16, 937–941 (2020)

[12] C. Johnson, B. Knighton, and J. Johnson, "Distinguishing Nonlinear Terahertz Excitation Pathways with Two-

Dimensional Spectroscopy," Phys. Rev. Lett. 122, 073901 (2019)