Large spin-phonon coupling and magnetically-induced phonon anisotropy in SrMO$_3$ perovskites ($M=$V,Cr,Mn,Fe,Co)

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First-principles calculations reveal large zone-center spin-phonon coupling and magnetically-driven phonon anisotropy in cubic perovskites SrMO$_3$ ($M=$V,Cr,Mn,Fe,Co). In particular, the frequency and splitting of the polar Slater mode is found to depend strongly on magnetic ordering. The coupling is parameterized in a crystal-structure-dependent Heisenberg model and its main features seen to arise from the Goodenough-Kanamori rules. This coupling can be expected to produce distinct low-energy alternative phases, resulting in a rich variety of coupled magnetic, structural and electronic phase transitions driven by temperature, stress, electric field and cation substitution.

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Multiferroic phases, which exhibit multiple orderings such as spontaneous polarization, magnetization, and strain, are currently the subject of much active research. The main interest lies not in the coexistence of the orderings in the same material but rather, in the couplings between the orderings. In improper multiferroics such as TbMnO$_3$, the principal symmetry broken by spontaneous polarization, and conversely, spins are invariant under inversion, spin-orbit interaction and is extremely small for all but the highest atomic number elements. Spontaneous polarization is invariant under time reversal symmetry, the principal symmetry broken by spontaneous magnetization, and conversely, spins are invariant under inversion, the principal symmetry broken by spontaneous polarization. In improper multiferroics such as Tb$_2$MnO$_4$, complex magnetic ordering breaks inversion symmetry and produces polarization, but the induced polarization is tiny. Moreover, the frustration needed to produce this magnetic ordering leads to low transition temperatures, while higher operating temperatures are needed for practical applications.

On the other hand, certain changes in interatomic distances and bond angles can have a large effect on exchange couplings, leading to changes in magnetic ordering energies. Systems exhibiting this magnetostructural coupling can be efficiently identified by first-principles calculations of the change in phonon frequency with magnetic order, referred to as spin-phonon coupling. Systems where the energy of these structural changes is comparable to the change in magnetic energy can have large responses to applied fields and the possibility of coupled phase transitions. For example, in TmTiO$_3$ and SrMnO$_3$, it was found that as a result of spin-phonon coupling, a ferromagnetic phase with a ferroelectric polar distortion is competitive in energy with the bulk antiferromagnetic paraelectric phase, leading to a coupled phase transition driven by epitaxial strain.

In this paper, we report a systematic first-principles study of the spin-phonon coupling of zone-center polar phonons in the cubic perovskites SrMO$_3$ ($M=$V,Cr,Mn,Fe,Co), with results for non-magnetic SrTiO$_3$ included for comparison. For all magnetic materials studied, the Slater-type phonon mode is found to exhibit the largest spin-phonon coupling, as measured by the frequency shift between the FM and G-AFM ordered phases. Further study of SrMnO$_3$ and SrCoO$_3$, which show the largest shifts, reveals pronounced magnetically-induced phonon anisotropy. This large spin-phonon coupling is parameterized with a crystal-structure-dependent Heisenberg model and analyzed with the help of the Goodenough-Kanamori rules. Experimentally observable consequences of the spin-phonon coupling are discussed, in particular the possibility of low-energy alternative phases and coupled phase transitions as a function of applied fields, stress, and cation substitution.

First-principles calculations were performed using density-functional theory within the generalized gradient approximation GGA+$U$ method with the Perdew-Burke-Ernzerhof parameterization as implemented in the Vienna Ab Initio Simulation Package (VASP). We use the Dudarev implementation with on-site Coulomb interaction $U$=2.5 eV and on-site exchange interaction $J_H$=1.0 eV to treat the localized 3d electron states. The value of $U$ for Mn was adjusted to 2.7 eV to fit the experimental magnetic moment of 2.6±0.2 $\mu_B$ for SrMnO$_3$. For Ti, we use $U = 0$. The projector augmented wave (PAW) potentials explicitly include 10 va-
and 1 × (3 for V (3 numbers. We obtained the modes at sampling was not included, so that the phonon wavevectors in supercells with the zone-center phonon frequencies of the ideal cubic perovskite reference structures with various magnetic or-
etic ordering type and band gap (in eV), compared with experimental information. The lowest energy magnetic orderings are reported in Table I and compared with measurement in the para-
magnetic phase. If the system is metallic, the gap is reported as m. The relative energies ΔE of alternative magnetic order-
slations specified by the letter in parentheses (in meV/atom) are computed at the given computed lattice constant. The experi-
mentally determined ordering temperatures Tc (in K) are included. Experimental data for SrVO3 is from Refs. 18,19 for SrCrO3 from Ref. 20, for SrMnO3 from Refs. 15,16, for SrFeO3 from Refs. 22,23, for SrCoO3 from Ref. 24, and for SrTiO3 from Refs. 23,24.

| a0          | order | gap  | ΔE  | Tc  |
|-------------|-------|------|-----|-----|
| SrVO3 3.88(3.85) F(SDW) m(m) 37(G) 85 K | | | | |
| SrCrO3 3.86(3.82) C(C) m(m) 7(G) 53(F) 40 K | | | | |
| SrMnO3 3.85(3.81) G(G) 0.45(i) 86(F) 233 K | | | | |
| SrFeO3 3.89(3.85) F(hel) m(m) 220(G) 134 K | | | | |
| SrCoO3 3.84(3.83) F(F) m 258(G) 305 K | | | | |
| SrTiO3 3.95(3.91) N(N) 1.8(3.3) - - | | | | |

The zone-center phonon frequencies of the ideal cubic perovskite reference structures with various magnetic or-
derings were computed using the frozen phonon method as 
ferred electrons for Sr (4s24p65s2), 6 for oxygen (2s22p4), 13 for V (3s23p63d44s1), 12 for Cr (3p63d54s1), 13 for Mn (3p63d54s2), 14 for Fe (3p63d64s1), and 9 for Co (3d84s1).

The computed ground state cubic lattice parameters and magnetic orderings are reported in Table I and com-
pared with experimental information. The lowest energy magnetic ordering is calculated in all cases except SrVO3 and SrFeO3, which are observed to have ferromagnetic spin density wave and complex helical or-
dering, respectively, not included in the first-principles analysis. The computed relative energies of higher-
energy magnetic orderings are reported and are seen to correlate roughly with the experimentally-observed magnetic-ordering temperatures given in Table I. The computed lattice constants are larger than experimental values by about 1%, as typical for GGA calculations of oxides. Consistent with experiment, all the magnetic compounds are found to be metallic except for SrMnO3, which has a computed gap of 0.45 eV, comparable to that

| SrTiO3 (d3) | SrVO3 (d3) | SrCrO3 (d3) |
|-------------|------------|-------------|
| non-mag.    | G-AFM      | G-AFM       |
| Slater 130 i | 329 290    | 287 187     |
| Last 144    | 148 147    | 156 145     |
| Axe 508     | 541 546    | 525 512     |

| SrMnO3 (d3) | SrFeO3 (d3) | SrCoO3 (d3) |
|-------------|------------|-------------|
| G-AFM      | G-AFM      | G-AFM       |
| Slater 120 i | 248 231    | 176 203     |
| Last 165    | 148 150    | 155 154     |
| Axe 475     | 486 506    | 508 498     |

In Table II we report the computed zone-center polar phonon frequencies for FM and G-AFM ordering. The phonons are labeled according to the character of the eigenmode. The Slater mode involves the oscillation of the B-cation against the oxygen-octahedron network. This is the soft mode which is closely associated with the ferroelectric instability in perovskites such as PbTiO3 and KNbO3. The Last mode involves the oscillation of the A-cation against the oxygen-octahedron network. It is this mode which is the soft mode for A-site ferroelec-
tricity in perovskites such as PbTiO3 or BiFeO3. The Axe mode, at the highest frequency, corresponds to distortion of oxygen octahedra.

While the Last and the Axe mode frequencies are, as would be expected from their eigenmode character, relatively insensitive to the B-site d-occupancy and magnetic ordering, the Slater mode shows a dramatic shift with change in d-occupation from compound to compound, and with change in magnetic ordering for a given compound. The Slater modes are highest in frequency for M=V (d1), M=Cr (d2) and M=Fe (d3); with cubic symmetry t2g-eg splitting, these cases involve partially occupied sublevels. For M=Mn (d3) and M=Co (d3), the Slater modes are substantially lower in frequency. The frequency shifts of the Slater mode between FM and G-AFM ordering are more than 100 cm−1 for SrCrO3, SrMnO3 and SrCoO3. In SrVO3 and SrFeO3, though the shift is smaller than for the other compounds, it is still significantly larger than for the other two modes. The low frequencies and the large magnetic ordering shifts in SrMnO3 and SrCoO3 lead, in fact, to ferroelectric insta-
ilities in the FM and G-AFM orderings, respectively. However, in each case these are not the lowest energy magnetic orderings, and thus the ground state structure does not exhibit a polar distortion. Next, we computed the polar phonon frequencies with two lower-symmetry magnetic orderings for SrMnO3 and SrCoO3, the two sys-
tems with the largest frequency shift with magnetic or-

| SrTiO3 (d3) | SrVO3 (d3) | SrCrO3 (d3) |
|-------------|------------|-------------|
| non-mag.    | G-AFM      | G-AFM       |
| Slater 130 i | 329 290    | 287 187     |
| Last 144    | 148 147    | 156 145     |
| Axe 508     | 541 546    | 525 512     |

| SrMnO3 (d3) | SrFeO3 (d3) | SrCoO3 (d3) |
|-------------|------------|-------------|
| G-AFM      | G-AFM      | G-AFM       |
| Slater 120 i | 248 231    | 176 203     |
| Last 165    | 148 150    | 155 154     |
| Axe 475     | 486 506    | 508 498     |
Each magnetic ordering and atomic displacement pattern can be characterized by the $B$ spins and atomic displacements of $B$ and oxygen relative to the line $B-O-B$: same spin and transverse displacement (FT), opposite spin and transverse displacement (AT), same spin and longitudinal displacement (FL) and opposite spin and longitudinal displacement (AL). For SrMnO$_3$, low frequency is primarily associated with the FT bonds, and to a lesser extent the AL bonds, which predominate in $A(z)$ magnetic ordering with displacements along the $z$ direction. On the other hand, for SrCoO$_3$ low frequency is associated with the AT bonds.

For a precise quantitative description of the spin-phonon coupling, we use the model parameterization of Ref. 31. The magnetic interactions are described by a Heisenberg model for the spins on the $B$ site$^{33,34}$, with exchange couplings determined by the computed energy differences between selected magnetic orderings. The coupling to the lattice originates from the dependence of the exchange coupling parameters on the atomic positions. Thus, changes in atomic displacement patterns result in changes in magnetic ordering energies; conversely, changes in magnetic orderings result in changes in the energetics of atomic displacements, in particular the interatomic force constants, producing the spin-phonon coupling.

For the cubic magnetic perovskite compounds considered here, the model energy is written $E = E_0 + E_{ph} + E_{spin}$. $E_0$ is the energy of the paramagnetic cubic perovskite structure. The phonon term $E_{ph} = \frac{1}{2} \sum_{\alpha \alpha'} K_{\alpha \alpha'} u_{\alpha} u_{\alpha'}$ is written here to include only primitive-perovskite cell zone-center modes, so that $\tau$ indexes the five atoms in the unit cell and $\alpha$ indicates the Cartesian direction of the sublattice displacement $\vec{u}_\alpha$.

$$E_{spin} = -\sum_{i \neq j} J_{ij} S_i \cdot S_j (S = 3/2),$$

where $i$ and $j$ index the $B$ site spins, is the Heisenberg model for the magnetic ordering energy. The exchange couplings are included up to third neighbors to reproduce the relative magnetic ordering energies in the cubic reference structure $\vec{u}_\tau = 0$. For SrMnO$_3$, this yields $J_1 = 3.1$ meV/f.u., $J_2 = 0.16$ meV/f.u. and $J_3 = 0.0027$ meV/f.u. For SrCoO$_3$, $J_1 = 8.8$ meV/f.u., $J_2 = 0.59$ meV/f.u. and $J_3 = 0.69$ meV/f.u. The decay with interspin spacing is considerably less rapid in SrCoO$_3$ than in SrMnO$_3$, as expected for a metallic system. In the following, we will consider the atomic-displacement dependence only for the first two neighbor interactions.

To investigate the spin-phonon coupling, we expand the model energy in the sublattice displacements $\vec{u}_\tau$. For spin configurations of sufficiently high symmetry, including the five configurations considered here, the first order terms vanish. At second order, the full force constant

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FIG. 1: (Color online) Computed frequencies for the Slater mode(s) for various magnetic orderings of cubic SrMnO$_3$, with results for SrCoO$_3$ given in parentheses. Arrows represent atomic displacements. Black and shaded circles represent up and down spins on the magnetic $B$-site in $ABO_3$ perovskites; small open circles represent oxygen atoms. Frequencies are given in cm$^{-1}$.
matrix $\tilde{K} = \partial^2 E / \partial u_{1} \partial u_{1}$ is given by

$$\tilde{K}_{\tau \sigma \tau' \sigma'} = \sum_{i \neq j} J''_{ij, \tau \sigma \tau' \sigma'} < \tilde{S}_{i} \cdot \tilde{S}_{j} >$$

with $J''_{ij, \tau \sigma \tau' \sigma'} = \partial^2 J_{ij, \tau \sigma} / \partial u_{ij, \tau \sigma}$. By symmetry, the $15 \times 15$ matrices $J''_{ij}$ are block diagonal, with nonzero elements only for sublattice displacements $u_{x}$ and $u_{y}$ along the same Cartesian direction. Furthermore, cubic symmetry relates the $5 \times 5$ block for displacements of one choice of $ij$ and Cartesian displacement direction to the blocks for other choices of $ij$ and Cartesian displacement direction, so that there are only four independent blocks: two for first neighbor exchange couplings ($z$-displacement blocks $J''_{x}$ and $J''_{y}$, with $J''_{y}$ related to $J''_{x}$) and for next nearest neighbors ($J''_{xy}$ for displacements along $z$ and exchange couplings within the $xy$ plane, and $J''_{xz}$ for displacements along $z$ and exchange couplings to spins at greater or lower $z$). For the spin configurations considered, the force constant matrices have the same block diagonal form as the $J''$ matrices and can be compactly expressed in terms of $J''$ $z$-displacement blocks as follows:

$$[\tilde{K}^{F}(\tilde{z})] = \begin{bmatrix} 1 & -9/2 & -9/2 & -9/2 & -9/2 & -9 \ 1 +9/2 & 9/2 & 9/2 & -9/2 & -9 \ 1 +9/2 & -9/2 & -9/2 & -9 \ 1 +9/2 & -9/2 & -9/2 & -9/2 & -9 \ 1 +9/2 & -9/2 & -9/2 & -9 \ 1 +9/2 & -9/2 & -9/2 & -9/2 & -9 \ \end{bmatrix}$$

where $\tilde{K}^{F}$, $\tilde{K}^{C}$, $\tilde{K}^{C}(x,y)$, $\tilde{K}^{A}(z)$ are $5 \times 5$ blocks of the full force constant matrices. Using first-principles computations for these matrices, we can determine the $J''$ blocks and $K$, the force constant matrix for paramagnetic ordering $< \tilde{S}_{i} \cdot \tilde{S}_{j} > = 0$.

Table III shows $J''_{x}$ and $J''_{y}$ $5 \times 5$ $z$-displacement blocks for SrMnO$_{3}$ and SrCoO$_{3}$. $O_{x}$ and $O_{y}$ denote the equatorial oxygens in the line $B-O-B$ along $x$ and the equatorial oxygen in the line $B-O-B$ along $y$, respectively.

From these matrices, we find that the large spin-phonon coupling noted for SrMnO$_{3}$ and SrCoO$_{3}$ can be mainly attributed to the nearest neighbor exchange interaction submatrix $J''_{1x}$, specifically the transverse displacement of the $B$ cations and oxygen atoms in the $B-O-B$ bond along $x$. For a more detailed discussion, we diagonalized the $J''_{1x}$ matrices. Eigenvalues of the $J''_{1x}$ block for SrMnO$_{3}$ are $(0.42,-0.04,-0.01,0.005,0.000)$ with eigenvector $(0.00,0.76,-0.62,0.06,-0.21)$ for the largest eigenvalue. A phonon with this displacement pattern thus would exhibit the maximum spin-phonon coupling, explaining the large effect for the Slater mode. The fact that the four of the five eigenvalues are close to zero allows us to approximate the atomic-displacement-dependent part of $J_{1x}$ using this single eigenvector:

$$\Delta J_{1x} \sim 0.066 [(u_{Mn} - u_{O_{x}}) + \frac{1}{3}(u_{Mn} - u_{O_{y}})]^2.$$

The bond angle reduction represented by the first term makes the main contribution to the spin-phonon coupling, with the bond length change represented by the second term being a secondary contribution.

For SrCoO$_{3}$, the analysis is very similar. Eigenvalues of the $J''_{1x}$ of SrCoO$_{3}$ are $(-0.54,0.013,0.005,-0.003,0.000)$ with eigenvector $(0.01,0.78,-0.56,0.03,-0.26)$ for the largest eigenvalue. Again, the other eigenvalues are close to zero, allowing the approximation

$$\Delta J_{1x} \sim -0.093 [(u_{Co} - u_{O_{x}}) + \frac{1}{3}(u_{Co} - u_{O_{y}})]^2.$$

As for SrMnO$_{3}$, the two terms represent the bond-angle reduction and bond-length change contributions, which for SrCoO$_{3}$ are negative rather than positive.

The importance of the two terms in SrMnO$_{3}$ can be qualitatively understood using the Goodenough-Kanamori rules. The magnetic exchange coupling $J$ is given by $J \sim \tau^2 / (\Delta - J_{H})$ where $\tau$ is the hopping integral, which is proportional to the effective wavefunction overlap between the two cations through their shared oxygen,
\( \Delta \) is the energy difference between oxygen and \( B \)-cation orbitals and \( J_H \) is the Hund coupling. Reduction of the bond angle \((\angle \Delta^2 \sim (u_B - u_{O_2})^2)\) decreases the hopping integral \( t \), which reduces the magnitude of the exchange coupling \( J \). Also, displacement of the apical oxygens \( O_2 \) towards the \( B \) cation should shift the \( B \)-cation and \( O_2 \) orbital energy level in opposite directions due to electrostatics; the resulting decrease in the magnitude of \( J \) arising from the change in \( \Delta \). For \( \text{SrCoO}_3 \), ferromagnetism can be explained by analogy to the Zener double exchange (DE) mechanism with high-spin CO \( d^6 \) ions and ligand holes of 1/3 per oxygen antiferromagnetically coupled to the Co spin, with the mobile holes favoring ferromagnetic alignment of the cobalt spins. If the \( d \rightarrow p \) matrix element is decreased by a reduction in bond angle, or the change-transfer gap is increased by displacement of the apical oxygen, this will decrease the magnitude of the magnetic exchange coupling.

While, as discussed above, the Slater mode maximizes the spin-phonon coupling, the other polar modes show very little change with magnetic ordering. The Axe mode consists mainly of \( O_2 \) displacements, which reduce the \( B-O_2 \) bond length without changing the \( B-O_2-B \) bond angles. The first term does not contribute and the change in \( J \) is much smaller, corresponding to a change only of \( \Delta \). The Last mode, which is a displacement of \( A \)-site cation with respect to the \( B \)-O6 network, does not change the relevant bond angles or bond lengths, and both terms are negligible.

The large spin phonon coupling for the Slater mode found from first principles can be experimentally observed in bulk samples by changing the magnetic ordering. In the paramagnetic phase, application of a magnetic field slightly increases alignment of the spins, leading to a phonon frequency shift that is rather small. For example, a mean field theory calculation for \( \text{SrMnO}_3 \) gives a shift of approximately 0.1 cm\(^{-1} \) with a field of 5 T at \( T_N \). A much more dramatic shift can be observed by changing the temperature through the magnetic phase transition. As the magnetic ordering changes from paramagnetic above the magnetic ordering temperature to the low-temperature ordered phase, the change in the spin correlations produces a substantial shift in phonon frequency that is roughly half the \( G \)-AFM-FM splitting. Indeed, motivated by these first principles results, far IR measurements have been made on \( \text{SrMnO}_3 \), showing the expected hardening of the Slater mode on cooling through \( T_N = 250 \) K.

Another readily measurable physical property is the magnetodielectric effect. For example, in \( \text{La}_2\text{MnNiO}_6 \), an applied magnetic field shifts the critical temperature of a phase transition at which the dielectric constant jumps by about 10%, producing a large magnetodielectric response between the two temperatures. In addition, magnetically-induced anisotropy could be directly observed by measuring phonon splittings in a material that has a \( C \)-AFM bulk phase, for example \( \text{SrCrO}_3 \). In this material, a large coupling between the magnetic moment and a breathing phonon in a hypothetical \( G \)-AFM phase has been noted from first principles.

In thin films and superlattices, the large spin-phonon coupling can produce a coupled magnetic-ferroelectric phase transition with epitaxial strain as polarization-strain coupling increases the instability of the polar mode for non-ground-state magnetic ordering (it should be noted that other perturbations, such as compositional substitution, could also be effective). An epitaxial-strain-induced multiferroic (ferromagnetic-ferroelectric) phase based on this mechanism was identified from first principles investigation in \( \text{EuTiO}_3 \) and subsequently experimentally confirmed. First-principles investigation of the epitaxial-strain phase diagram of \( \text{SrMnO}_3 \) has shown an analogous multiferroic phase, with higher ordering temperature. In \( \text{SrCoO}_3 \), with a ferromagnetic metallic bulk state, the polarization-strain coupling increases the ferroelectric instability of the insulating antiferromagnetic phase, driving a coupled magnetic-ferroelectric metal-insulator transition with epitaxial strain, which has been the subject of a first-principles study. These systems are expected to exhibit desirable functional behavior at the phase boundary associated with switching between the two phases by applied fields or stresses.

In summary, we have presented a first-principles investigation of the spin-phonon coupling in the Sr \( A \)-site perovskite compounds \( \text{SrMO}_3 \) \((M=\text{V},\text{Cr},\text{Mn},\text{Fe},\text{Co})\). The coupling is largest for the Slater phonons, especially for \( \text{SrMnO}_3 \) and \( \text{SrCoO}_3 \) which show large frequency shifts with changes in magnetic ordering and magnetically induced phonon anisotropy. We show that this behavior can be qualitatively understood on the basis of Goodenough-Kanamori rules. The computed spin-phonon coupling can be experimentally investigated directly through measurement of the phonon frequency shift through the magnetic transition. Other consequences include the possibility of coupled phase transitions with epitaxial strain or compositional substitution and desirable functional behavior for systems at the phase boundary. Thus, computation of spin-phonon coupling can be a valuable screening tool in the first-principles design of novel functional and multifunctional materials.

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