



Large spin-phonon coupling and magnetically induced phonon anisotropy in SrMO_3 perovskites ($M = \text{V, Cr, Mn, Fe, Co}$)

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First-principles calculations reveal large zone-center spin-phonon coupling and magnetically-driven phonon anisotropy in cubic perovskites SrMO_3 ($M = \text{V, Cr, Mn, Fe, Co}$). In particular, the frequency and splitting of the polar Slater mode is found to depend strongly upon 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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I. INTRODUCTION

Multiferroic phases, which exhibit multiple orderings such as spontaneous polarization, magnetization, and strain, are currently the subject of much active research.^{1,2} The main interest lies not in the coexistence of the orderings in the same material, but rather in the couplings between the orderings. In combination with direct control of the orderings by macroscopic fields and stresses, these couplings lead to physical properties including linear magnetoelectric response, magnetodielectric response, and cross-switching of magnetization by electric fields or polarization by magnetic fields. Furthermore, multiferroic systems can exhibit coupled phase transitions in which the system transforms from the bulk phase to an alternative low-energy phase with distinct ordering of multiple types, with functional behavior at the phase boundary arising from switching between the two phases. This behavior offers both fundamental scientific interest and the possibility of novel multifunctionality for technological applications such as sensors, actuators and information storage.

One major challenge is that magnetostructural coupling is generally quite small. Magnetocrystalline anisotropy, which measures the coupling of the direction of the spin magnetization to the lattice, depends on the 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_2MnO_5 ,³ 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 calculations⁴⁻⁷ 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 EuTiO_3 (Ref. 8) and SrMnO_3 ,⁶ 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 ($M = \text{V, Cr, Mn, Fe, Co}$), with results for nonmagnetic 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.⁹ 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.

II. METHOD

First-principles calculations were performed using density-functional theory within the generalized gradient approximation GGA+ U method¹⁰ with the Perdew-Becke-Erzenhof parametrization¹¹ as implemented in the *Vienna Ab Initio Simulation Package* (VASP-4.6).^{12,13} We use the Dudarev¹⁴ 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 $2.6 \pm 0.2 \mu_B$ for SrMnO_3 .¹⁵ For Ti, we use $U = 0$. The projector augmented wave (PAW) potentials¹⁶ explicitly include 10 valence electrons for Sr ($4s^2 4p^6 5s^2$), 6 for oxygen ($2s^2 2p^4$), 13 for V ($3s^2 3p^6 3d^4 4s^1$), 12 for Cr ($3p^6 3d^5 4s^1$), 13 for Mn ($3p^6 3d^5 4s^2$), 14 for Fe ($3p^6 3d^7 4s^1$), and 9 for Co ($3d^8 4s^1$). The zone-center phonon frequencies of the ideal

cubic perovskite reference structures with various magnetic orderings were computed using the frozen phonon method in supercells with $\sqrt{2} \times \sqrt{2} \times \sqrt{2}$, $\sqrt{2} \times \sqrt{2} \times 1$, $1 \times 1 \times 2$, and $1 \times 1 \times 1$ primitive perovskite cells for G -AFM, C -AFM, A -AFM, and FM, respectively. Spin-orbit coupling was not included, so that the phonon wave vectors for the primitive perovskite cell remain good quantum numbers. We obtained the modes at $\vec{q} = 0$ by uniformly displacing all atoms related by translation symmetries of the primitive perovskite structure. For each supercell, Monkhorst-Pack (M-P) k -point meshes¹⁷ were chosen to obtain phonon frequencies converged to within a few cm^{-1} .

III. RESULTS AND DISCUSSION

The computed ground-state cubic lattice parameters and magnetic orderings are reported in Table I and compared with experimental information. The lowest energy magnetic ordering is correctly computed in all cases except SrVO_3 (Ref. 19) and SrFeO_3 ,²² which are observed to have ferromagnetic spin density wave and complex helical ordering, 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 SrMnO_3 , which has a computed gap of 0.45 eV, comparable to that found in a previous study.²⁷

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 mode²⁸ involves the oscillation of the B -cation against the oxygen-octahedron network. This is the

TABLE I. Cubic perovskite lattice constant a_0 (in Å), magnetic ordering type and band gap (in eV), compared with available experimental data (in parentheses). The lattice constant was calculated for the computed magnetic type given in the table, except for that of SrCrO_3 , which was computed for G -type ordering and compared with measurement in the paramagnetic phase. If the system is metallic, the gap is reported as m . The relative energies ΔE of alternative magnetic orderings specified by the letter in parentheses (in meV/f.u.) are computed at the given computed lattice constant. The experimentally determined ordering temperatures T_c (in K) are included. Experimental data for SrVO_3 is from Refs. 18 and 19, for SrCrO_3 from Ref. 20, for SrMnO_3 from Refs. 15 and 21, for SrFeO_3 from Refs. 22 and 23, for SrCoO_3 from Ref. 24, and for SrTiO_3 from Refs. 25 and 26.

	a_0	order	gap	ΔE	T_c
SrVO_3	3.88(3.85)	F(SDW)	$m(m)$	37(G)	85 K
SrCrO_3	3.86(3.82)	C(C)	$m(m)$	7(G),53(F)	40 K
SrMnO_3	3.85(3.81)	G(G)	0.45(i)	86(F)	233 K
SrFeO_3	3.89(3.85)	F(hel)	$m(m)$	220(G)	134 K
SrCoO_3	3.84(3.83)	F(F)	m	258(G)	305 K
SrTiO_3	3.95(3.91)	N(N)	1.8(3.3)	–	–

TABLE II. Computed IR-active polar phonon frequencies (cm^{-1}) of G -AFM and FM states in cubic SrMO_3 perovskites. The calculations were done with computed lattice constants given in Table I.

	SrTiO_3 (d^0)		SrVO_3 (d^1)		SrCrO_3 (d^2)	
	nonmag.		G -AF	FM	G -AF	FM
Slater	130	i	329	290	287	187
Last	144		148	147	156	145
Axe	508		541	546	525	512
	SrMnO_3 (d^3)		SrFeO_3 (d^4)		SrCoO_3 (d^5)	
	G -AF	FM	G -AF	FM	G -AF	FM
Slater	120	122	248	231	176	i
Last	165	165	148	150	155	154
Axe	475	486	506	505	508	498

soft mode which is closely associated with the ferroelectric instability in perovskites such as BaTiO_3 and KNbO_3 . The Last mode²⁹ involves the oscillation of the A cation against the oxygen-octahedron network. It is this mode which is the soft mode for A -site ferroelectricity in perovskites such as PbTiO_3 or BiFeO_3 . The Axe mode,³⁰ 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 $M = \text{V}$ (d^1), $M = \text{Cr}$ (d^2), and $M = \text{Fe}$ (d^4); with cubic symmetry t_{2g} - e_g splitting, these cases involve partially occupied sublevels. For $M = \text{Mn}$ (d^3) and $M = \text{Co}$ (d^5), 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 SrCrO_3 , SrMnO_3 , and SrCoO_3 . In SrVO_3 and SrFeO_3 , 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 SrMnO_3 and SrCoO_3 lead, in fact, to ferroelectric instabilities 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 SrMnO_3 and SrCoO_3 , the two systems with the largest frequency shift with magnetic ordering. Specifically, we considered C type, with AFM ordering in the xy plane and FM ordering along the normal direction, giving periodicity $\vec{q} = (\pi/a, \pi/a, 0)$, and A type, with FM ordered planes ordered antiferromagnetically along the normal direction, giving periodicity $\vec{q} = (0, 0, \pi/a)$. The magnetic ordering and the frequencies of the associated Slater modes are shown in Fig. 1. The symmetry lowering due to the C - and A -AFM orderings lifts the degeneracy of the Slater mode in each case by a considerable amount. This frequency splitting, which occurs even without any symmetry-lowering relaxation of the crystal

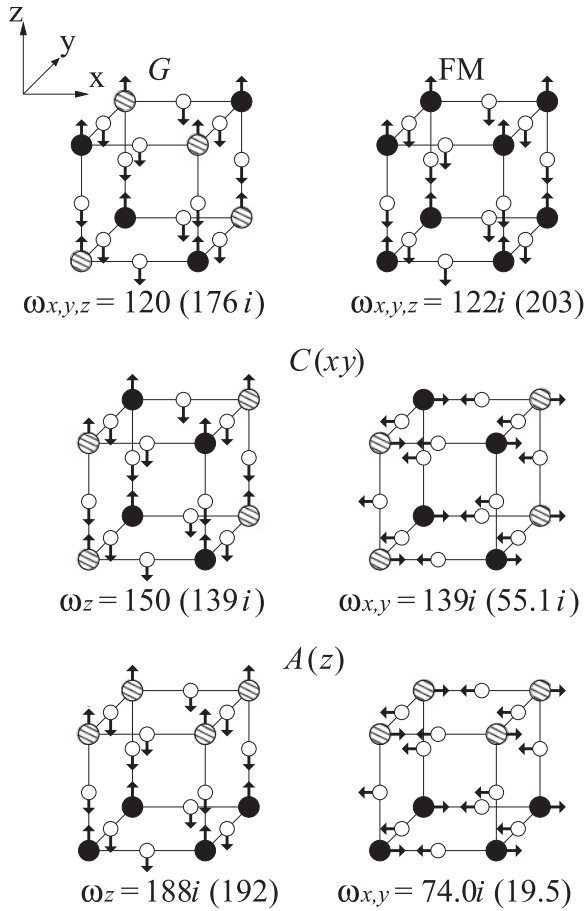


FIG. 1. Computed frequencies for the Slater mode(s) for various magnetic orderings of cubic SrMnO₃, with results for SrCoO₃ given in parentheses. Arrows represent atomic displacements. Black and shaded circles represent up and down spins on the magnetic *B* site in ABO₃ perovskites; small open circles represent oxygen atoms. Frequencies are given in cm⁻¹.

structure, is referred to as magnetically-induced phonon anisotropy.^{31,32} In *C(xy)*-AFM SrMnO₃, the Slater mode with polarization along *z* is much stiffer than that with polarization in the plane, which is unstable; the splitting is reversed in SrCoO₃, with both modes unstable. In *A(z)*-AFM SrMnO₃ both modes are unstable though the ferroelectric instability along the *z* direction is favored, while in SrCoO₃ the Slater mode with polarization along *z* is much stiffer than that with polarization in the plane, which has a very low frequency.

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 SrMnO₃, 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 SrCoO₃ low frequency is associated with the AT bonds.

For a precise quantitative description of the spin-phonon coupling, we use the model parametrization 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, atomic displacements 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 $E = E_0 + E_{\text{ph}} + E_{\text{spin}}$. E_0 is the energy of the paramagnetic cubic perovskite structure. The phonon term $E_{\text{ph}} = \frac{1}{2} \sum_{\tau\alpha\tau'\alpha'} K_{\tau\alpha\tau'\alpha'} u_{\tau\alpha} u_{\tau'\alpha'}$ is written here to include only primitive-perovskite cell zone-center modes, so that τ indexes the five atoms in the unit cell, and α indicates the Cartesian direction of the sublattice displacement \vec{u}_{τ} . $E_{\text{spin}} = -\sum_{i \neq j} J_{ij} \vec{S}_i \cdot \vec{S}_j$ ($S = 3/2$), 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 SrMnO₃, 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 SrCoO₃, $J_1 = 8.8$ 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 SrCoO₃ than in SrMnO₃, 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}_{τ} . 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 matrix $\tilde{K} = \partial^2 E / \partial u_{\tau\alpha} \partial u_{\tau'\alpha'}$ is given by

$$\tilde{K}_{\tau\alpha\tau'\alpha'} = K_{\tau\alpha\tau'\alpha'} - \sum_{i \neq j} J''_{ij, \tau\alpha\tau'\alpha'} u_{\tau\alpha} u_{\tau'\alpha'} (\vec{S}_i \cdot \vec{S}_j),$$

with $J''_{ij, \tau\alpha, \tau'\alpha'} \equiv \frac{\partial^2 J_{ij}}{\partial u_{\tau\alpha} \partial u_{\tau'\alpha'}}$. By symmetry, the 15×15 matrices J''_{ij} are block diagonal, with nonzero elements only for sublattice displacements \vec{u}_{τ} and $\vec{u}_{\tau'}$ along the same Cartesian direction. Furthermore, cubic symmetry relates the 5×5 block for displacements for 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''_{1x} and J''_{1z} , with J''_{1y} related to J''_{1x}), and two for next nearest neighbors ($J''_{2\parallel}$ for displacements along z and exchange couplings within the xy plane, and $J''_{2\perp}$ 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:

$$\begin{bmatrix} \tilde{K}^F(\hat{z}) \\ \tilde{K}^G(\hat{z}) \\ \tilde{K}^C(\hat{z}) \\ \tilde{K}^C(\hat{x}) \\ \tilde{K}^A(\hat{z}) \\ \tilde{K}^A(\hat{y}) \end{bmatrix} = \begin{bmatrix} 1 & -9/2 & -9/2 & -9/2 & -9 & -18 \\ 1 & +9/2 & +9/2 & +9/2 & -9 & -18 \\ 1 & +9/2 & +9/2 & -9/2 & -9 & +18 \\ 1 & +9/2 & -9/2 & +9/2 & +9 & 0 \\ 1 & -9/2 & -9/2 & +9/2 & -9 & +18 \\ 1 & -9/2 & +9/2 & -9/2 & +9 & 0 \end{bmatrix} \begin{bmatrix} K \\ J''_{1x} \\ J''_{1y} \\ J''_{1z} \\ J''_{2\parallel} \\ J''_{2\perp} \end{bmatrix},$$

where \tilde{K}^F , \tilde{K}^G , $\tilde{K}^{C(xy)}$, and $\tilde{K}^{A(z)}$ are 5×5 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 $\langle \vec{S}_i \cdot \vec{S}_j \rangle = 0$.

Table III shows J''_{1x} and J''_{1z} 5×5 z -displacement blocks for SrMnO₃ and SrCoO₃. 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 SrMnO₃ and SrCoO₃ 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 SrMnO₃ 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 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:

$$\Delta J_{1x} \sim 0.066[(u_{\text{Mn}} - u_{\text{O}_x}) + \frac{1}{3}(u_{\text{Mn}} - u_{\text{O}_z})]^2.$$

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 SrCoO₃, the analysis is very similar. Eigenvalues of the J''_{1x} of SrCoO₃ 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

$$\Delta J_{1x} \sim -0.093[(u_{\text{Co}} - u_{\text{O}_x}) + \frac{1}{3}(u_{\text{Co}} - u_{\text{O}_z})]^2.$$

As for SrMnO₃, the two terms represent the bond-angle reduction and bond-length change contributions, which for SrCoO₃ are negative rather than positive.

The importance of the two terms in SrMnO₃ can be qualitatively understood using the Goodenough-Kanamori rules.⁹ The magnetic exchange coupling J is given by $J \sim t^2/(\Delta - J_H)$, where t is the hopping integral, which is proportional to the effective wave function overlap between the two cations through their shared oxygen, Δ is the energy difference between oxygen and B -cation orbitals, and J_H is the Hund coupling. Reduction of the bond angle $[(\Delta\theta)^2 \sim (u_B - u_{\text{O}_x})^2]$ decreases the hopping integral t , which reduces the magnitude of the exchange coupling J . Also, displacement

of the apical oxygens O_z toward the B cation should shift the B cation and O_z orbital energy level in opposite directions due to electrostatics, the resulting decrease in the magnitude of J arising from the change in Δ . For SrCoO₃, ferromagnetism can be explained by analogy to the Zener double exchange (DE) mechanism^{35,36} 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 Co spins.³⁷ If the d - 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.³⁸

While, as discussed above, the Slater mode maximizes the spin-phonon coupling, the other polar modes show very little change with magnetic ordering.^{6,39,40} The Axe mode consists mainly of O_z displacements, which reduce the B -O_z bond

TABLE III. J''_{1x} and J''_{1z} of SrMnO₃ and SrCoO₃. Unit is in 10^{-4} eV/Å².

J''_{1x}	Sr	Mn	O _x	O _y	O _z
Sr	-61	-14	17	70	-9
Mn	-14	2400	-2000	310	-650
O _x	17	-2000	1500	-43	530
O _y	70	310	-43	-270	-80
O _z	-9	-650	530	-80	210
J''_{1x}	Sr	Co	O _x	O _y	O _z
Sr	-7	-40	66	-17	-5
Co	-40	-3300	2400	-170	1100
O _x	66	2400	-1700	49	-820
O _y	-17	-170	49	83	50
O _z	-5	1100	-820	50	-330
J''_{1z}	Sr	Mn	O _x	O _y	O _z
Sr	-30	-75	26	26	54
Mn	-75	-1500	220	220	1200
O _x	26	220	-150	-8	-80
O _y	26	220	-8	-150	-80
O _z	54	1200	-80	-80	-1100
J''_{1z}	Sr	Co	O _x	O _y	O _z
Sr	27	46	-11	-11	-53
Co	46	-1100	250	250	540
O _x	-11	250	150	19	-410
O _y	-11	250	19	150	-410
O _z	-53	540	-410	-410	330

length without changing the $B-O_x-B$ bond angles. The first term does not contribute, and the change in J is much smaller, corresponding to a change only of Δ . The Last mode, which is a displacement of A -site cation with respect to the $B-O_6$ 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 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 SrMnO_3 ,⁴⁰ showing the expected hardening of the Slater mode upon cooling through $T_N = 250 \text{ K}$.

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.⁴¹ 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 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.⁴²

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 EuTiO_3 (Ref. 8) and subsequently experimentally confirmed.⁴³ First-principles investigation of the epitaxial-strain phase diagram of SrMnO_3 has shown an analogous multiferroic phase, with higher ordering temperature.⁶ In 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.⁴⁴ 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.

IV. CONCLUSIONS

We have presented a first-principles investigation of the spin-phonon coupling in the Sr A -site perovskite compounds SrMO_3 ($M = \text{V, Cr, Mn, Fe, Co}$). The coupling is largest for the Slater phonons, especially for SrMnO_3 and 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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