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Lattice stability of Sr_2RuO_4 under pressure

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We report a density functional study of the pressure dependence of the zone-center A_g Raman phonon modes and the zone-boundary Σ_3 octahedral rotational mode in Sr_2RuO_4. We find that the octahedral rotation does not soften significantly under compression and thus will not be destabilized with moderate hydrostatic pressure. However, nonhydrostatic pressure, in particular compression in the basal plane, is found to be effective in softening the rotational mode.

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The discovery of triplet,[1,2] presumably *p*-wave, superconductivity in highly pure samples of the layered perovskite Sr_2RuO_4 has led to a considerable body of work aimed at elucidating the properties of this unique material. One particularly interesting issue is the relationship between the triplet superconductivity ($T_c \sim 1.35$ K) and nearby magnetic phases. In fact, perovskite derived ruthenates $(Sr,Ca)_{n+1}Ru_nO_{3n+1}$ with nominally Ru^{4+} in an octahedral O environment display an richly varied set of physical properties.

The end members of the Sr series, $SrRuO_3$ and Sr_2RuO_4, are, respectively, an itinerant ferromagnet[3–7] and, as mentioned, an unconventional superconductor, with triplet pairing symmetry,[1,2] possibly of magnetic origin.[8–11] The Fermi surface and momentum-dependent spin fluctuations play key roles in the pairing in such scenarios for superconductivity. The spin fluctuations are, however, quite complicated, as the material is near both ferromagnetism and antiferromagnetism.[9] The corresponding Ca end points $CaRuO_3$ and Ca_2RuO_4, which differ structurally from the corresponding Sr compounds only by moderate lattice distortions, are a highly renormalized paramagnetic metal and an antiferromagnetic Mott insulator, respectively.[12–18] The structural differences between the Sr and Ca compounds are due to tilts and rotations of the RuO_6 octahedra, as is usual in perovskites when the *A*-site cations with different ionic radii are substituted.

The multilayer Ruddlesden-Popper compounds in the series show a wide variety of magnetic orderings, metal insulator transitions, and unusual transport properties. Most notable, perhaps, is a metamagnetic quantum critical point in very clean samples of the bilayer compound $Sr_3Ru_2O_7$.[19] Not surprisingly, strong magnetoelastic effects are found and have been emphasized both theoretically[7,20–22] and experimentally.[22] The simplest such coupling is to the rotation of the oxygen octahedra. Such rotations are presumably responsible for most of the differences between the Sr-based materials and the corresponding Ca compounds[7,20] (note that Ca has a smaller ionic radius than Sr, leading to larger rotations in the Ca compounds).

Sr_2RuO_4 is most unusual for a layered perovskite material, in that it actually occurs in the ideal, $I4/mmm$ undistorted tetragonal structure. Inelastic neutron scattering experiments[23] showed that the Σ_3 phonon branch exhibits a sharp drop near the zone boundary (1/2,1/2,0), where it corresponds to the RuO_6 octahedral rotation about *c*. That is, Sr_2RuO_4 is close to but not at a rotational instability. The frequency of the rotational mode is only modestly *T* dependent; i.e., there is no signature of mode softening. The mode shows little dispersion along $(0.5\,0.5\,\xi)$, indicating two-dimensional (2D) character with almost no coupling between rotations in neighboring layers. However, the mode does become unstable at the surface where it freezes in. Calculations imply an enhanced proximity to magnetism at the surface due to the rotation,[22] although at present it seems that the magnetic fluctuations do not order.[24] Fang and Terakura showed, in fact, that freezing in the rotational mode strongly favors ferromagnetism.[20] An intriguing possibility is that the enhanced tendency to ferromagnetism, associated with rotations at the surface, is related to the enhanced (~ 3 K) interfacial superconductivity seen in Ru-rich samples. Plainly, it is of great interest to elucidate the interplay of structural distortions, magnetism, and superconductivity in Sr_2RuO_4.

Intriguingly, alloying Ca into Sr_2RuO_4 does destabilize the Σ_3 zone-boundary phonon,[12,13,18] leading to frozen-in rotations about *c* starting at $\sim 25\%$ Ca. With increasing Ca content, the rotation angle increases as does the low-temperature susceptibility until an apparent critical point is reached at $\sim 75\%$. Unfortunately, superconductivity is destroyed upon substitution of even very small amounts of Ca, presumably due to scattering associated with the alloy. Another possibility is to use pressure to tune the proximity to magnetism. In fact, the strong dispersion of the Σ_3 branch and the moderately high frequencies of phonons associated with distortion of RuO_6 octahedra implies that these units are reasonably stiff in Sr_2RuO_4. In such cases, pressure often leads to a destabilization of the rotational modes[25] as has been emphasized recently in the context of Pb-based piezoelectrics.[26] In particular, these materials contain stiff TiO_6 octahedra, which are associated with this pressure depedence, and we note that the ionic radii of the Ti^{4+} in those materials and the Ru^{4+} in Sr_2RuO_4 are similar. However, one should also note that the high degree of covalency in Sr_2RuO_4 may be expected to soften the repulsive interactions between Ru and O ions, while one might expect that the Sr-O repulsion may be stiffer than the Pb-O repulsion. These two factors combined would suggest perhaps less tendency towards rotational instabilities under pressure.

Neutron powder diffraction investigations of the thermal expansion and compressibility of Sr_2RuO_4 show that the temperature dependence of the Ru–apical-O [O(2)] bond length is linear with no structural anomaly at least in the pressure range (0–0.62 GPa) studied.[27] Under pressure, the Ru-O(2) apical bond is much harder than, e.g., the Cu-O(2) bond in $(La,Sr)_2CuO_4$. This is based on structural refinements. At present, phonon dispersions have not been measured under pressure. From a theoretical point of view, one would expect that Sr_2RuO_4 would become further from magnetism under modest pressure, due to band broadening related to a shortening of the bond lengths. However, if the Σ_3 phonon does soften under pressure, eventually it will become unstable, leading to an increased tendency towards magnetism and perhaps an eventual magnetic ordering. This is a particularly interesting possibility, as it involves no alloying and therefore offers the possibility of tuning the proximity to magnetism towards the critical point in clean Sr_2RuO_4 samples. Here we report density functional studies of the pressure dependence of the Σ_3 zone-boundary phonon as well as some other phonons to see whether this is possible. Unfortunately, we find that this rotational mode does not soften significantly under pressure, with the conclusion that practical hydrostatic pressures will not destabilize this mode. However, nonhydrostatic compression of the basal plane is found to be effective.

The calculations were done in the local density approximation (LDA), using the general potential-linearized augmented-plane-wave (LAPW) method with local orbitals,[28,29] as in previous calculations for this material.[30] LAPW sphere radii of 2.1, 1.95, and 1.65 Bohr were used for Sr, Ru, and O, respectively. The Hedin-Lundqvist exchange correlation potential was employed.[31] The basis set consisted of a well-converged set of standard LAPW basis functions with additional local orbital functions to relax linearization errors for the Ru $4d$ and O $2s$ and $2p$ states and to include the Sr and Ru semicore states. Calculations were done at ambient pressure 0.62 GPa and a high pressure of 2.4 GPa.

The tetragonal lattice parameters c and a at 0.62 GPa were taken from the experimental refinements of Chmaissem and co-workers.[27] We extrapolated these data to 2.4 GPa assuming linear compression of a and c. In particular, we used $a=7.294$, 7.284, and 7.260 bohr at 0, 0.62, and 2.4 GPa, respectively, and $c=24.028$, 23.990, and 23.872 Bohr at 0, 0.62, and 2.4 GPa, respectively. Of course, the compressibility is probably not linear up to this pressure. Still, while the calculation may not correspond to a true pressure of 2.4 GPa, it does allow us to elucidate the trend in the Σ_3 phonon frequency up to high pressure. In principle it is possible to obtain the stress as a function of lattice parameters and internal coordinates directly from LDA calculations, e.g., using the stress theorem.[32,33] However, this was not done, and considering the typical LDA errors of 1%–3% in the predicted equilibrium lattice parameters of materials, such a calculation may not be helpful in the pressure range we consider. The two internal structural parameters $z_{O(2)}$ and z_{Sr}, corresponding to the apical O height and the Sr height (see Fig. 1 for the structure), were determined by energy minimization using the calculated density functional forces at each pressure. As a by-product of this minimization, we obtained the two corresponding A_g Raman frequencies. Once the values of z_{O2} and z_{Sr} were found, the frequency of the octahedral rotation mode was obtained by calculating the total energy as a function of this coordinate and fitting to a polynomial. There is a moderate discrepancy of 30 cm^{-1} between the calculated Σ_3 frequency and the experimental value at ambient pressure. We carefully checked the convergence of the result with respect to the basis set size and zone sampling, and so ascribe this difference to the normal LDA errors in soft modes (note that since we calculate quantities proportional to the square of the frequency, if these have a fixed error, then the error in the frequency goes roughly as the inverse of the frequency). Results are given in Tables I and II. As may be seen, the three modes calculated show only a modest pressure dependence, and in particular the Σ_3 rotational mode is nearly pressure independent.

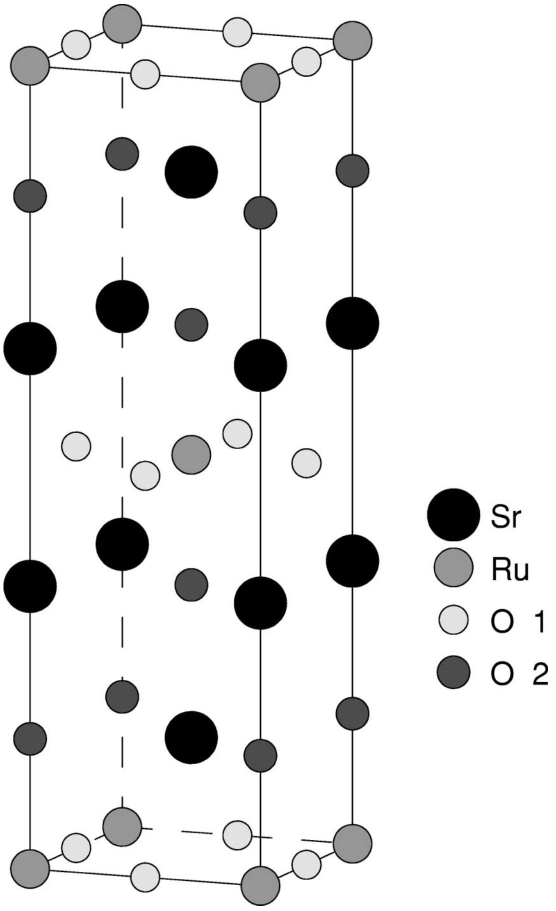

FIG. 1. Body-centered tetragonal layered structure of Sr_2RuO_4.

In perovskites, the pressure dependence of rotational modes is governed by a competition between the stiffness of the octahedra (favoring softening under pressure) and the ionic repulsion between the O and the *A*-site, in this case Sr, ions (favoring stiffening under pressure). These evidently balance in Sr_2RuO_4. The question then is whether there is any nonchemical way to upset this balance and thereby induce the rotation. The softness of the Sr Raman modes suggests one possibility. Symmetry does not allow harmonic

TABLE I. Calculated frequencies ω and displacement patterns for the full-symmetry Raman zone-center modes of Sr_2RuO_4 at ambient pressure, 0.62 GPa and 2.4 GPa. The lower-frequency mode is Sr in character, while the upper mode is apical O derived.

P (GPa)	ω (cm^{-1})	Displacement pattern (arbitrary units)		Character
		z_{Sr}	z_O	
0.0	191	−0.107	−0.007	Sr
	541	−0.004	0.250	O
0.62	193	−0.106	−0.008	Sr
	547	−0.003	0.250	O
2.4	196	−0.106	−0.020	Sr
	465	−0.009	0.249	O

TABLE II. Calculated Σ_3 zone-boundary $(0.5,0.5,0)2\pi/a$ phonon frequencies ω as a function of pressure P.

P(GPa)	Frequency (cm^{-1})
0.0	111
0.62	110
2.4	119

coupling of the full-symmetry Raman modes to the Σ_3 mode. However, uniaxial compression along the c axis should couple to the Sr height and thus may be expected to alter the balance between Sr-O and internal octahedral interactions. Uniaxial strain has already been suggested as a method of tuning the proximity to a quantum critical point in the weak itinerant ferromagnet Sc_3In.[34] In order to check whether such an approach can be useful in Sr_2RuO_4, we performed calculations with a compression along c of approximately 6.5% keeping the a lattice parameter fixed. The Sr and apical O heights were optimized. Interestingly, the Raman mode associated with the apical O is strongly stiffened to 730 cm^{-1}. However, we find that the rotational mode is strongly disfavored by this compression; the Σ_3 frequency becomes 214 cm^{-1}. As expected from this result, extending c beyond its experimental value leads to a softening of the Σ_3 mode. A 6.5% extension (with relaxation of z_{O2} and z_{Sr}) yields an unstable Σ_3 mode ($\omega = 80i$ cm^{-1}). Unfortunately, such a large negative uniaxial strain is not realizable in practice. However, since the dependence of the Σ_3 mode on hydrostatic pressure is weak, one might expect that the same softening could be achieved by compression in the basal plane. To verify this we performed calculations with c held at its experimental value and a compressed by 2.3%. As before, z_{O2} and z_{Sr} were relaxed. The calculated Σ_3 frequency was $\omega = 58i$ cm^{-1}, i.e., a borderline instability of this branch.

The above results show that the Σ_3 mode, corresponding to rotation of the RuO_6 octahedra in Sr_2RuO_4, can be softened by nonhydrostatic pressure. This would be a very interesting thing to do considering the unanswered questions about the interplay between triplet superconductivity and magnetic fluctuations in this material. However, it should be emphasized that the nonhydrostatic pressures required are not small, and so this would be a difficult experiment. Using the uniaxial compressibilities from the measurements of the a and c lattice parameters under pressure,[27] one may estimate that if stress is applied only in the basal plane (so that c will expand according to Poisson's ratio), a compression of a of about 1.5% would be needed to destabilize the rotational mode. Perhaps some information can be obtained by compressing a superconducting powder or a composite of superconducting Sr_2RuO_4 particles with another material, so that the individual particles are subjected to randomly nonhydrostatic conditions.[35] Another possibility would be to grow Sr_2RuO_4 films on mismatched substrates, but this would require the development of methods for growing sufficiently clean films to obtain superconductivity—something that has yet to be demonstrated.

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