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Structural stability of Sr_2RuO_4

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The stability of low-lying phonon modes in the layered perovskite superconductor Sr_2RuO_4 has been investigated by inelastic neutron scattering. The Σ_3 branch, which ends at the (0.5 0.5 0) zone boundary in the mode corresponding to the RuO_6 octahedron rotation around c, exhibits a sharp drop near the zone boundary. This clearly indicates that Sr_2RuO_4 is close to a rotational instability. Although the frequency of the rotational mode depends only little on temperature, it anomalously broadens with increasing temperature. A flat dispersion of the rotation branch along c reveals pronounced two-dimensional character; there is almost no coupling between rotational deformations of neighboring layers. In contrast, the tilt mode in La_2CuO_4 that drives the tetragonal-to-orthorhombic phase transition does not exhibit any anomalous behavior in Sr_2RuO_4.
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I. INTRODUCTION

The discovery of superconductivity in the layered perovskite Sr_2RuO_4 stimulated a considerable research effort.[1] Among the large number of oxide perovskites, there are only a few noncuprate superconducting compounds known besides Sr_2RuO_4 ($T_c \sim 1.35$ K): $SrTiO_3$ and the $(Ba/K)(Bi/Pb)O_3$ family, and among all these Sr_2RuO_4 is the only one that has a layered structure.

Sr_2RuO_4 crystallizes in the K_2NiF_4 structure isostructural to La_2CuO_4. As the latter and more generally most of the perovskites exhibit structural phase transitions, it was tempting to search for such features also in Sr_2RuO_4. These transitions are characterized by rotations of the metal-oxygen octahedron: in the La_2CuO_4-T phase family there is a series of low-temperature phases where the rotation axes are always parallel to the ab planes, therefore, these transitions are characterized by tilts of the octahedron.[2] The structural instability in the La_2CuO_4 compounds is reflected in a low-frequency zone boundary Σ_4 mode,[2] which will be called ''tilt mode'' throughout this paper. The softening manifests itself in the dispersion of the lowest optic Σ_4 branch at fixed temperature as well as in the temperature dependence of the zone-boundary frequency. The rotation of the octahedron around the c axis that corresponds to a zone-boundary Σ_3 mode, does not lead to a structural distortion in La_2CuO_4; nevertheless, its frequency is found to be quite low too.[3] This mode of Σ_3 symmetry will be called ''rotational mode.'' The related mode in the R_2CuO_4-T' phase compounds [for the T' phase the irreducible representations are not exactly the same as for the T phase due to the difference in the out-of-plane oxygen (O2) position], which corresponds to the rotation of the CuO_4 square around c, was found to become unstable against a long-range structural distortion in compounds with small rare earths.[4] Furthermore, a similar type of distortion was observed in the compounds Sr_2RhO_4 (Ref. 5) and Sr_2IrO_4 (Ref. 6) which are both isostructural to Sr_2RuO_4 and La_2CuO_4.

Several studies using powder or single-crystal diffraction could not reveal a structural phase transition of either type in Sr_2RuO_4.[7–10] Nevertheless, it appeared interesting to analyze the dispersion of the related branches by inelastic neutron scattering. Moreover, the fact that Sr_2RuO_4 remains undistorted to low temperatures is favorable for the analysis of the lattice dynamics.

II. EXPERIMENT

Two series of experiments were performed on the triple axis spectrometer 2T installed at the Orphée reactor. Double focusing pyrolitic graphite (002) crystals were used as monochromator and analyzer; a pyrolitic graphite filter was placed between sample and analyzer. In order to take advantage of the focusing arrangement, we choose open collimations. The energy resolution of this configuration corresponds roughly to a conventional spectrometer with 37′ collimation throughout. The samples were cooled in a closed-cycle refrigerator.

For the first series a crystal of about 30 mm^3 volume (crystal I) was investigated in the (100)/(010) and (110)/(001) scattering planes; several scans were recorded by tilting the sample crystal out of these scattering planes. For the second series a much larger crystal of about 300 mm^3 volume (crystal II) was available, which was oriented in the (100)/(001) and (110)/(001) geometries. Both crystals were grown by a floating zone technique.[11]

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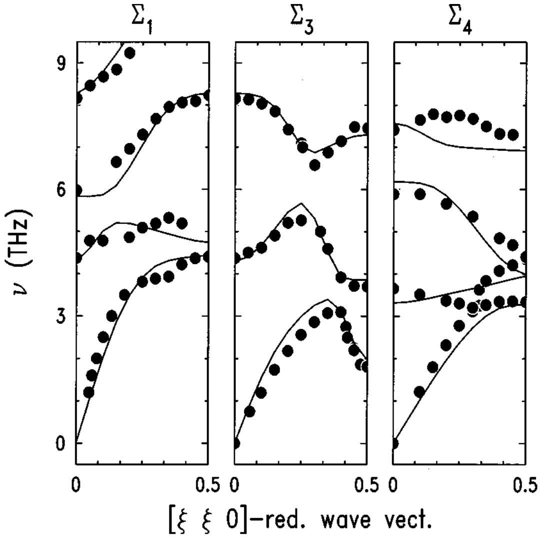

FIG. 1. Low-frequency part of the phonon dispersion along [110]. Only the branches corresponding to the Σ_1, Σ_3, and Σ_4 representations (for explanations see text) are shown; the symbols denote the experimental data and the lines the frequencies calculated by a shell model.

TABLE I. Parameters of the shell model used to describe the low-frequency part of the phonon dispersion in Sr_2RuO_4. The short-range forces are described by Born-Mayer potentials and van der Waals terms: $V(r)=A\ \exp(r/R_0)+C/r^6$, with A, R_0, and C given in table. Z, Y, and K are the ionic and shell charges and the core-shell force constants (in plane and out of plane in the case of Ru). The metallic character is taken into account by screening described by the Lindhard function. In addition angular forces were incorporated for the O1-Ru-O1 and O2-Ru-O2 triples forming a 180 degrees angle. These angular forces are 7016 and 11 605 dyn/cm, respectively.

	A (eV)	R_0 (Å)	C (eV Å^6)
Sr-O1	1810	0.318	
Sr-O2	2209	0.318	
Ru-O1	2954	0.260	
Ru-O2	3871	0.260	
O1-O1	2000	0.284	−100
O1-O2	2000	0.284	−100
O2-O2	2000	0.284	−100
	Z	Y	K_s (10^{-6} dyn/cm)
Sr	1.99	5.60	3.6
Ru	2.56	0.63	8.0/2.0
O1	−1.51	−3.32	1.8
O2	−1.76	−2.75	1.8

III. RESULTS AND DISCUSSION

The phonon dispersion relation of Sr_2RuO_4 consists of 21 branches covering a frequency range of about 20 THz; only three zone center frequencies have been determined by the Raman technique.[12] Our experiments were focussed on the modes related to possible structural phase transitions and, hence, emphasized the [110] direction (Σ branches); results are shown in Fig. 1. However, a great amount of data was also collected in the other main symmetry directions, which together with the Raman results allowed us to refine a shell model for Sr_2RuO_4. The calculated frequencies for the Σ direction are included in Fig. 1.

For the description of the dispersion curves we have tried to use parameters close to the transferable shell model presented in Ref. 13; the model parameters describing the low-frequency part fairly well are given in Table I. In addition to the screened shell model it was necessary to incorporate angular forces for Ru-O interactions. Details of the model, which still evolves with the knowledge of the high-energy branches actually investigated, will be discussed in a forthcoming paper.

Some low-lying modes were observed for the Δ and Λ branches approaching the zone-boundary R-point (001) and (100), which are symmetrically equivalent. However, this behavior is due to the long c axis and the layered character of the structure. It should not be considered anomalous.

The 21 branches along [110] can be divided into four different representations Σ_1-Σ_4. There are 7 branches with Σ_1 symmetry—they include the longitudinal acoustic (LA) modes—3 of Σ_2 symmetry, 5 of Σ_3 symmetry including the transverse acoustic (TA) modes polarized along [1 − 10], and 6 of Σ_4 symmetry, which contain the TA modes polarized parallel to the c axis. The tilt deformation in the La_2CuO_4 compounds has Σ_4 symmetry; this mode is degenerated in the sense that the mode at (0.5 0.5 0) describing a tilt around [1 − 10] has the same frequency as the one at (0.5 −0.5 0), which describes the tilt around [1 1 0]. Therefore, all tilt deformations around any in-plane axis are equivalent. The pronounced soft mode behavior seen in the dispersion of La_2CuO_4 is absent in Sr_2RuO_4. This is inferred from the dispersion of the lowest optic Σ_4 branch in Fig. 1, which starts from the E_g frequency at 3.7 THz. There is only a slight decrease of this branch at small q, but it stays flat beyond $\xi\sim0.2$ up to the zone boundary tilt mode (3.4 THz). The absence of any dispersion near the zone boundary and the relatively high frequency of the tilt mode indicates that Sr_2RuO_4 is far from a tilt instability.

A steep dispersion is observed near the rotational mode belonging to the Σ_3 representation, see Fig. 1. Here, a branch starting at the 8.2-THz E_u mode at the Γ point is softening continuously in the Brillouin zone. This softening, which becomes rather steep towards the zone boundary, leads to successive interactions with the first optic and the acoustic Σ_3 branches with a transfer of character. At the X point, (0.5 0.5 0), the rotational mode has the lowest frequency. This sharp dip in the dispersion curve is typical for a structural instability in perovskite compounds; it can be well described by the lattice dynamical model into which Born-Mayer potentials, screened Coulomb interactions, isotropic core shell inter-actions, and O-Ru-O angular forces were incorporated. Comparing to La_2CuO_4 one may assume that Sr_2RuO_4 does not experience the identical tilt instability, but appears to be rather close to an unstable octahedron rotation around the c axis.

The temperature dependence of the rotational mode was studied in two different geometries at the (2.5 1.5 0) reciprocal lattice vector. In Figs. 2(b) and 2(c) we show scans obtained in the (100)/(010) orientation, and those performed by tilting the sample out of the (110)/(001) orientation. In the

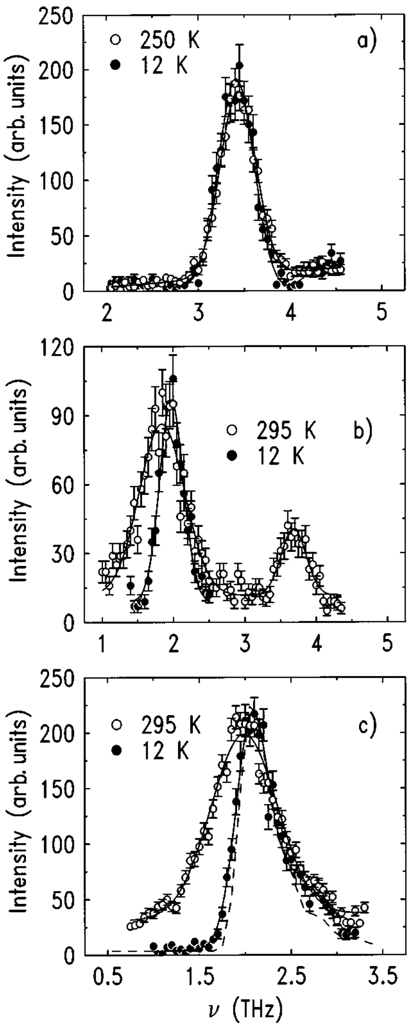

FIG. 2. Raw data scans across the rotation or tilt modes at different temperatures; the symbols denote the measured intensities and the solid lines fits by one or two Gaussians. The mode corresponding to the tilt around an axis parallel to the *ab* plane is investigated at (1.5 1.5 2); the scans at 250 K and at 12 K are shown in (a). The mode corresponding to the rotation around the *c* axis was analyzed at (2.5 1.5 0) in the (100)/(010) scattering geometry using crystal I, part (b), and in the (110)/(001) geometry by tilting out of the scattering plane using crystal II (c). In the latter orientation the vertical resolution of the spectrometer introduces a significant shift of the intensity maximum compared to the phonon frequency. This effect was calculated using the lattice dynamical model and the resolution function, the result is presented by the dashed line.

first orientation where the *c* axis stands perpendicular to the scattering plane, resolution effects are negligible; see Fig. 2(b). In the second orientation the $[1\ -1\ 0]$ direction is normal to the scattering plane. As the dispersion along this direction is rather steep (see Fig. 1) the relaxed vertical resolution of the spectrometer produces asymmetric peak profiles whose maximum intensity position is significantly shifted from the phonon frequency. Nevertheless, the observed intensity shape can well be described by folding the resolution function of the triple-axis spectrometer with the three-dimensional dispersion calculated by the lattice dynamical model. The dashed line shown in Fig. 2(c) corresponds to this calculation, it is fitted to the data with only two free parameters, a scale factor and a constant background.

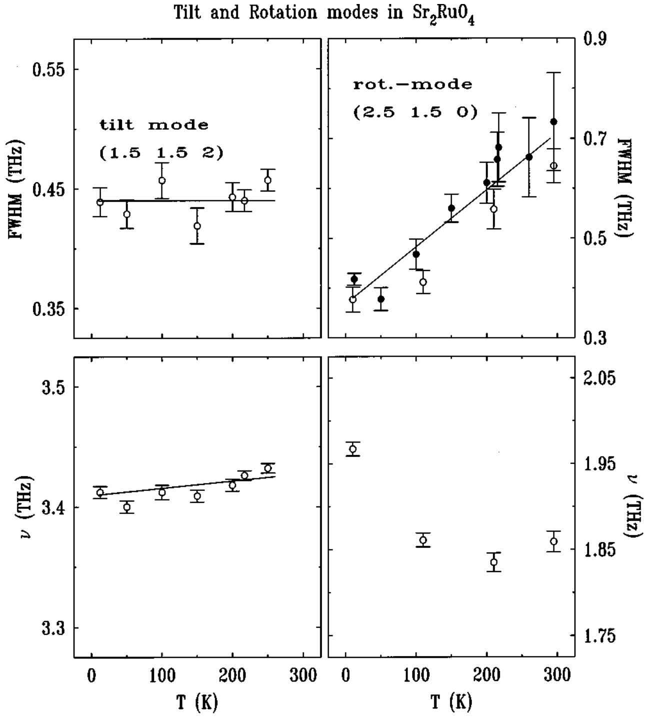

FIG. 3. The rotation and tilt mode frequencies and widths as a function of temperature. On the left side the results for the tilt around an in-plane axis are shown, and those for the *c*-axis rotation mode are presented on the right side.

There is only little temperature dependence of the frequency of the rotational mode; see Fig. 3. The mode hardens slightly on cooling in contrast to the expectation for a nearby structural instability which should cause some frequency softening. The observed small hardening may be considered as the usual behavior, as the thermal lattice contraction causes higher phonon frequencies at low temperatures. However, the increase of about 5% appears strong compared to the small thermal expansion, in addition, the increase only at low temperatures is astonishing. The temperature dependence of the tilt mode was investigated at (1.5 1.5 2): there is only a small (of the order of 1%) softening on cooling to 12 K in contrast to the pronounced softening in the La_2CuO_4 compounds.

Whereas the width of the tilt mode does not show any influence of the temperature, [see Figs. 2(a) and 3], we observe a strong effect for the broadening of the rotational mode; see Figs. 2(b), 2(c), and 3. At the lowest temperature, the observed phonon widths are only slightly larger than the experimental resolution. On heating the peaks become continuously broadened, as can be clearly seen in the raw scans performed in the two orientations; see Fig. 2. This anomalous broadening is certainly not due to some temperature change in the dispersion area, which is integrated by the resolution ellipsoid, since in both orientations the same effect is observed in spite of completely different resolution conditions. Furthermore, it appears unlikely that a strong change in the dispersion occurs without a similar impact on the *X*-point frequency itself. So, one should conclude that there is anomalous broadening due to an interaction with thermally activated quasiparticles.

The origin of the broadening might be purely structural, involving strongly anharmonic lattice dynamics close to a structural instability. However, even for an imminent but not condensing structural distortion one should expect the phonon softening on cooling, leading to an overdamped mode at low temperature. The suppressed ferroelectric transition in $SrTiO_3$ is the best known example for such behavior.[14] The observed broadening in Sr_2RuO_4 may be interpreted as an indication of electron-phonon coupling. A strong electron-phonon coupling for the rotational distortion is supported by the phase diagram of $Sr_2Ru_{1-x}Ir_xO_4$,[15] where the rotational mode is condensing in a long-range distorted structure for high In contents. Most interestingly, the transport properties in this series change from metallic to semiconducting behavior just at the structural phase boundary between the ideal K_2NiF_4 structure at small x and the distorted phase at high x. Already the occurrence of a structural phase transition in itself is astonishing as the ionic radii of Ru and Ir are almost identical.[16] Hence, it is impossible to explain the transition by bond length arguments only. Furthermore, Sr_2RuO_4 was found to be in good equilibrium within the K_2NiF_4 structure:[10] the analysis of the bond lengths via bond length–bond strength relations yields bond valence sums rather close to the expected values and, hence, indicates that the bond lengths are in equilibrium—nevertheless, Sr_2RuO_4 appears much closer to the rotational instability than La_2CuO_4, for example. Anomalous effects related to the c-axis rotational distortion were also reported for the T'-phase cuprates. There, the rotation of the CuO_4 squares appears to cause the suppression of superconductivity in several compounds.[17,18]

The structural transitions in Sr_2IrO_4 (Ref. 6) and in Sr_2RhO_4 (Ref. 5) result in a doubling of the c-lattice parameter; therefore, soft mode behavior is not expected at (0.5 0.5 0) but at (0.5 0.5 0.5). At room temperature and at 12 K, the dispersion of the rotational branch in Sr_2RuO_4 along c, i.e., along the zone boundary (0.5 0.5 ξ), was studied, the results are presented in Fig. 4. At low temperature the dispersion along c is found to be flat within the experimental accuracy of about 1%. Also, at room temperature one observes only a slight softening towards (0.5 0.5 0.5) of about 2%. The flat dispersion indicates that there is almost no coupling of the rotation distortion between nearest-neighbor or next-nearest-neighbor planes. Also, the width of the rotation modes along the zone boundary does not depend on the c component of the wave vector. Therefore, the rotational instability in Sr_2RuO_4 exhibits pronounced two-dimensional character, which is rather unusual for a structural feature. A similar behavior has been found in $KMnF_3$, which possesses the perovskite structure,[19] however, most of the perovskites show three-dimensional coupling of the octahedron rotations. The lack of interlayer coupling in Sr_2RuO_4 reflects the layered character of this material in contrast to the cubic perovskites. $KMnF_3$ might be exceptional due to a low ionic polarizability. The two-dimensional character of the short-range fluctuations in Sr_2RuO_4 may be essential for the understanding of a possible coupling to the electronic system. The extremely weak interlayer coupling should become relevant only when the three-dimensional transition into a low-symmetry phase occurs. Actually, the difference between the low-temperature space groups observed in the T'-phase cuprates[4] and in Sr_2IrO_4 (Ref. 6) and Sr_2RhO_4 (Ref. 5) consists just in the stacking scheme of the distorted planes. The difference in the out-of-plane oxygen position is sufficient to alter the interlayer coupling for the long-range distortion.

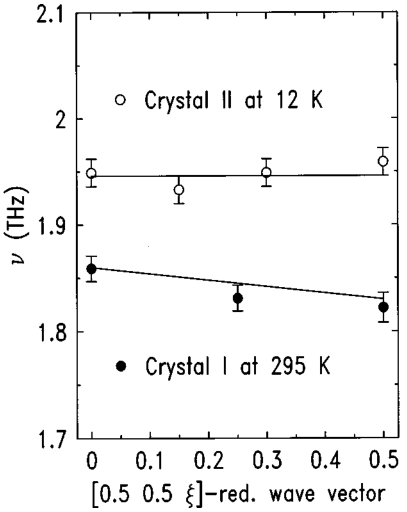

FIG. 4. Dependence of the rotation mode frequency on the q_c component. Open and closed circles denote the results obtained in the (100)/(010) and (110)/(001) scattering geometries, with crystal I at 295 K and with crystal II at 12 K, respectively. The latter data were corrected for the resolution-induced shifts.

IV. CONCLUSION

Concerning the structural stability significant differences between Sr_2RuO_4 and La_2CuO_4 are found. Whereas the cuprate is unstable against octahedron tilts around an axis parallel to the ab plane, the Ru compound does not present any indication of the tilt instability. In contrast, the steep dispersion of a branch with Σ_3 character towards the zone boundary reveals that Sr_2RuO_4 is close to an instability characterized by the octahedron rotation around the c axis. However, the origin of this instability remains unclear, as the bond distances observed in Sr_2RuO_4 agree well with the equilibrium values. It seems unlikely that this instability or the related structural transition in Ir-substituted compounds is explained by structural arguments only. In particular, the anomalous broadening of the rotation mode on heating points to a more complex mechanism.

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