Phonon anomalies at the magnetic phase transition in $SrRuO_3$

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Raman spectra of $SrRuO_3$ films grown epitaxially on $LaAlO_3$ substrate by a pulsed laser deposition have been measured. Phonon spectra showed an anomalous temperature dependence in the range of the magnetic phase transition indicating strong spin-lattice interaction. No sharp magnon lines were observed, but the broad continuum spectrum showed redistribution of intensity at the magnetic phase transition suggesting that multimagnon processes may contribute to the continuum.

The conductive metallic oxide $SrRuO_3$ has been of recent interest in technological applications.[1,2] Superconducting devices such as superconductor-ferromagnet-superconductor junctions $YBa_2Cu_3O_7$-$SrRuO_3$-$YBa_2Cu_3O_7$ have been fabricated.[3] These devices can be produced because $SrRuO_3$ grows epitaxially on a variety of oxide substrates and high-temperature superconductors, and vice versa. Single crystals of $SrRuO_3$ have previously been investigated by several groups.[4–6] $SrRuO_3$ exhibits a ferromagnetic transition between 150 and 160 K. However, the type of magnetic ordering has not been conclusively established. Magnetization measurements reveal a magnetic moment of about $1\mu_B$ per Ru atom. Here we apply the Raman-scattering technique to study the phonon spectra of this material as a function of temperature in the temperature range including the magnetic phase transition.

The $SrRuO_3$ films have been grown on (100) $LaAlO_3$ substrates (cubic approximation) by pulsed laser deposition. X-ray-diffraction measurements revealed good crystallinity. Since the {002} and {110} peaks of the $SrRuO_3$ are degenerate, it is difficult to determine the film orientation. The position of the weak nondegenerate peak (113) suggests that the film is oriented along {110}. The film has multidomain texture with alternating {110} and {002} directions in the plane. The distorted perovskite structure of $SrRuO_3$ is described by the orthorhombic space group D_{2h}^{16}.[1] There are four molecular formula units in the primitive cell. As follows from the nuclear site group analysis,[7] the following modes are active in Raman scattering: $5A_g+4B_{1g}+4B_{2g}+4B_{3g}$.

For the Raman studies the sample with dimensions approximately 5×5 mm was bonded by In to the cold finger of an optical cryostat. The spectra were taken by a Spex triple scanning spectrometer equipped with 1800 l/mm holographic gratings and detected by a cooled GaAs photomultiplier. For the excitations of the spectra 514.5 and 488.0 nm lines of Argon ion laser have been used. The laser beam was weakly focused by a cylindrical lens to a $\sim1\times3$ mm strip in order to avoid heating of the sample. Laser power incident on the sample was kept below 200 mW and no noticeable changes due to heating, such as increase of anti-Stokes scattering intensity or decrease of phonon frequencies, have been observed. The measurements were done in the usual backscattering geometry used for metallic samples. The instrumental linewidth was comparatively large, 10 cm^{-1}, due to very weak spectrum of the material.

Examples of phonon spectra at different temperatures without polarization analysis are presented in Fig. 1. Due to the multidomain structure of films and their complicated orientation on the substrate we could not study the polarization selection rules for the spectra. Six phonon modes superposed on the electronic background are clearly observed in the low-temperature spectra. As can be seen from Fig. 1, the phonon lines noticeably broaden, shift, and decrease in intensity as the temperature is increased. The experimental data on the phonon frequency shift as a function of temperature for the strongest intensity phonon peak are presented in Fig. 2. In the same

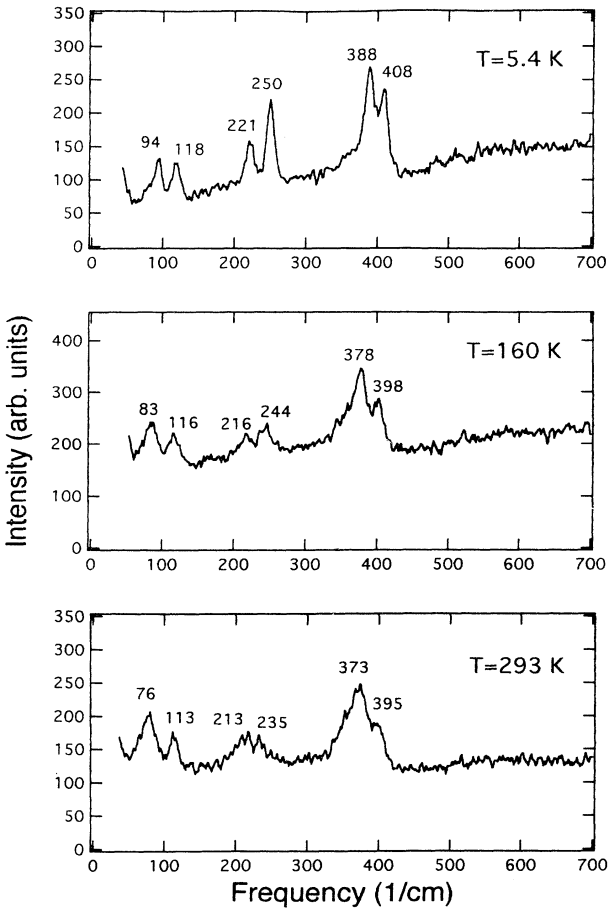

FIG. 1. Phonon Raman spectra of $SrRuO_3$ at different temperatures.

figure the calculated approximate frequency shift due to phonon anharmonicity for normal crystals without phase transitions is presented for comparison. In the calculations the lowest order contribution due to interaction of an optical phonon with two optical or acoustical phonons of equal energy was considered for simplicity and the values of anharmonic coefficients were chosen to fit the frequency values at 5 and 533 K. The following equation, applicable when phase transitions do not occur, has been used:[8]

$$\Delta(T)=a\left[\frac{1}{e^{\hbar\omega_a/kT}-1}+\frac{1}{2}\right], \tag{1}$$

where a is the third-order anharmonic coefficient and ω_a is equal to half the measured phonon frequency. More detailed calculations, which consider three- and four-phonon processes for the whole Brillouin zone, would show similar typical dependences in the studied temperature range where four-phonon processes due to quartic anharmonicity give a very small contribution.[8] Comparison of experimental and calculated dependences reveals an anomalous softening in a broad region around the Curie temperature. Similar anomalies were observed for the other five phonon branches active in Raman scattering, but the temperature dependences could not be followed accurately above the room temperature due to reduction of intensity of phonon lines, broadening and merging into electronic background.

Linewidths of phonons as function of temperature were difficult to measure because higher-energy phonon doublets practically converge into broad singlets above the phase transition. The lowest frequency phonon line at 94 cm^{-1} at 5 K could be followed through the phase transition and its full width at half height as a function of temperature is presented in Fig. 3. In order to determine the phonon linewidth we assumed that it had a Lorentzian profile; the Lorentzian linewidth was obtained from the Voight experimental profile.[9] The calculated linewidth dependence for a typical "normal" crystal without a phase transition is also presented for comparison. In these calculations, as before for the frequency shift, we included only three phonon processes, and assumed that the 94 cm^{-1} optical phonon decays into two 47 cm^{-1} acoustical phonons. We used the following equation, with the value of the anharmonic coefficient b chosen to fit the temperature range below magnetic phase transition:

$$\Gamma(T)=\Gamma_0+b\left[\frac{1}{e^{\hbar\omega_b/kT}-1}+\frac{1}{2}\right]. \tag{2}$$

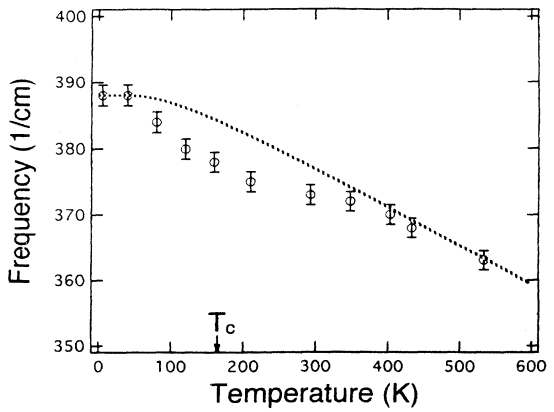

FIG. 2. Temperature dependence of optical phonon frequency of $SrRuO_3$. Dotted line corresponds to a typical dependence for normal crystals without phase transition [Eq. (1)]. The arrow indicates the temperature of the ferromagnetic phase transition.

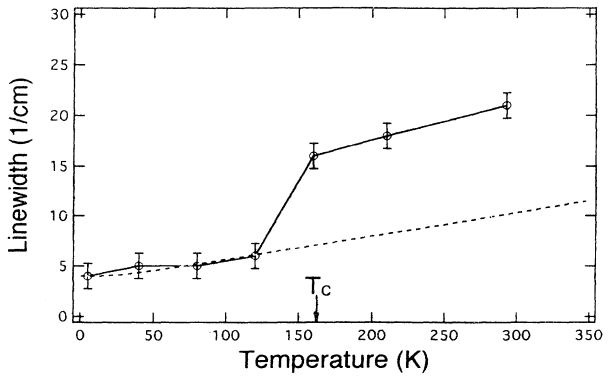

FIG. 3. Linewidth of the 94 cm^{-1} line as a function of temperature. Continuous line is a guide line only. The dashed line corresponds to a typical dependence for a crystal without phase transition [Eq. (2)].

Here Γ_0, line broadening due to defects, is equal to 3.2 cm^{-1}, $b=1.6$ cm^{-1}, and $\omega_b/2\pi=47$ cm^{-1}. As can be seen from Fig. 3, an anomalous step in the temperature dependence of the linewidth is observed in the range of the magnetic phase transition at 160 K. Presently we cannot explain the occurrence of a step rather than a maximum usually expected for a phase transition. Possibly the linewidth continues to be large after the phase transition due to interaction of this lowest frequency phonon mode with magnetic fluctuations still strong in a paramagnetic phase.

Additional anomalous behavior is observed in the peak intensity of the 250 cm^{-1} mode. It is well defined in the low-temperature spectra and it practically disappears at and above the temperature of the phase transition (Fig. 1). Weak traces of this line are still present at room temperature, however, so we attribute it to phonon excitations and not to one-magnon excitations. The experimentally observed ratio of the peak intensity of 250 cm^{-1} phonon to the intensity of the electronic background as a function of temperature is shown in Fig. 4.

As seen from Fig. 2, the phonon anomalies at T_c are rather broad which indicates that the phase transformation develops in wide temperature interval which is typical for second-order phase transitions in solids. The resistance anomaly is observed in the similar broad temperature range around T_c.[1] The anomalies in the phonon spectra due to magnetic ordering can be explained by magnon-phonon interaction. This interaction can be especially strong for phonon modes involving vibrations of ions participating in the exchange interaction. According to some models of magnetic order, all ions participate in the exchange interactions in $SrRuO_3$.[6] The softening and increase of damping of phonons in the vicinity of the magnetic phase transition may be attributed to scattering of phonons by spin fluctuations. The anomalous dependence of the peak intensity of phonon lines, especially of the 250 cm^{-1} line, on the magnetic order may be explained by the folding of the Brillouin zone of $SrRuO_3$ at the magnetic phase transition. The selection rules for Raman scattering in the magnetically ordered phase, which give strong intensity to the 250 cm^{-1} mode, are determined by a magnetic space group with a larger primitive cell. Similar effects of lattice distortion caused by magnetic ordering have been observed earlier in EuSe.[10,11]

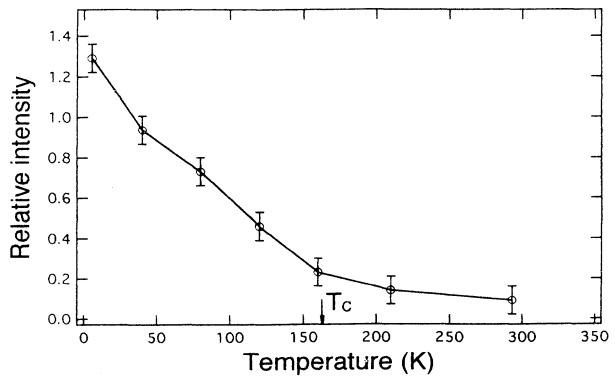

FIG. 4. Peak intensity of the 250 cm^{-1} line in relation to the intensity of the electronic continuum in the vicinity of the line as a function of temperature. Continuous line is a guide line only.

The quasicontinuous broad range Raman spectra at different temperatures obtained with 514.5 nm excitation without use of a polarization analyzer are shown in Fig. 5. The spectra were very similar with 488.0 nm excitation. As in the case of phonon spectra we were not able to measure the polarization selection rules due to multidomain structure of the sample and magneto-optical activity. The spectra are not corrected for the instrumental response and change in the absorption coefficient, which is necessary when spectra are taken in such a wide spectral range. The correction for absorption requires the knowledge of the optical constants of $SrRuO_3$ which are not available yet. Nevertheless, the difference in the spectra taken below and above phase transition can be easily noticed. The broad continuum spectrum is observed at 5 K. The noticeable redistribution of intensity with shift to the lower energy occurs as the temperature increases through T_c. Due to the complicated magnetic structure of $SrRuO_3$ and comparatively small changes of the spectrum at the phase transition it is difficult to extract the spin contribution to the continuum spectrum. Because there are four nonequivalent positions of Ru ions

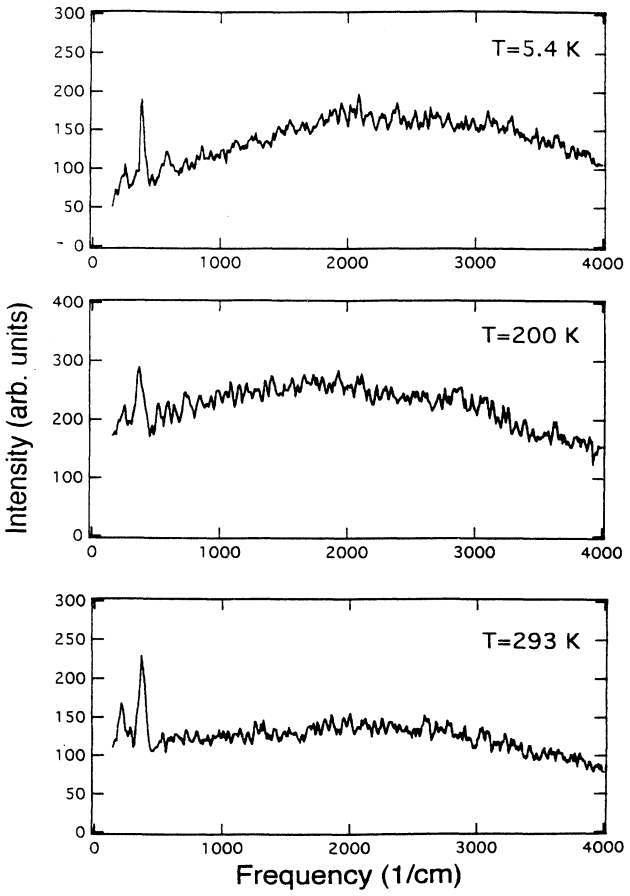

FIG. 5. Electronic Raman spectra of $SrRuO_3$ at different temperatures.

in the primitive cell, we should expect at least four magnon branches. The only features observed in $SrRuO_3$ which may be related to the magnetic scattering is a broad high-energy band. There is some similarity between magnetic scattering in $SrRuO_3$ and $RbNiF_3$,[12] also a complicated material which is ferrimagnetic with distorted perovskite structure containing six magnetic Ni ions in the primitive cell. A broad peak attributed to the two-magnon scattering, persisting in the spectrum above T_c, is observed in $RbNiF_3$.[12] Similarly, no sharp magnon lines are in $SrRuO_3$ spectra and only very broad electronic band persisting above T_c is observed. In difference from the spectrum of $RbNiF_3$,[12] the magnetic scattering in $SrRuO_3$ appears to have much larger bandwidth and energy. In this respect it is similar to the spectra of cuprate magnetic oxides related to high-temperature superconductors.[13,14] Very large linewidth of magnon bands and spread to high energy may be caused by strong damping of magnons due to interaction with free carriers and by contribution of resonant multimagnon processes involving more than two magnons.[14] It is important to note that resonant electronic interband and intraband transitions observed in other metallic oxides with perovskite-like structure[15] may also contribute to the continuum spectrum of $SrRuO_3$. Our data are not sufficient to separate magnetic contributions from intraband and interband electronic contributions.

In summary, we have shown evidence for magnon-phonon interactions in the temperature dependence of the phonon spectra over wide temperature range around the Curie temperature. A broad band of electronic excitations has been observed which is likely to include strongly damped multimagnon processes.

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