Raman scattering study of $Ru(Sr,La)_2GdCu_2O_8$

V. Damljanović, C. Ulrich, C. Bernhard, and B. Keimer
Max Planck Institute for Solid State Research, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

P. Mandal
Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Calcutta 700064, India

A. Krimmel and A. Loidl
Experimental Physics V, Center for Electronic Correlations and Magnetism, Augsburg University, D-86159 Augsburg, Germany
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We present a Raman scattering study of $Ru(Sr_{1-x}La_x)_2GdCu_2O_8$, a material that exhibits coexisting magnetic order and high-temperature superconductivity for $x=0$, but becomes semiconducting for $x=0.1$. A pronounced anomaly of an oxygen vibration at the magnetic transition temperature evolves smoothly through the superconductor-semiconductor transition. In contrast, a previously observed, broad low-energy mode disappears rapidly with increasing x, mirroring the rapid hole-concentration dependence of the net magnetization in the magnetically ordered state. We discuss these findings as possible indications of spin, charge, and orbital order of the Ru ions.

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I. INTRODUCTION

Both ruthenium oxides and copper oxides with layered perovskite structure have generated much attention by virtue of their intriguing physical properties. In both families of materials, unusual superconducting and charge-ordered states as well as magnetic field-induced phase transitions have been reported. $RuSr_2GdCu_2O_8$ is particularly interesting, because it contains both RuO_2 and CuO_2 layers stacked in an alternating fashion.[1–3] The material is superconducting with a maximum transition temperature T_c around 60 K. The superconducting state coexists with magnetic order[4] that sets in at much higher temperatures ($T_M \leq 160$ K). In zero magnetic field, the magnetic order parameter comprises both ferromagnetic and antiferromagnetic components, but antiferromagnetism is predominant.[5–8] The antiferromagnetic order vanishes in a modest magnetic field, while the net magnetization increases strongly. The phenomenology of $RuSr_2GdCu_2O_8$ has thus rekindled interest in the coexistence of superconductivity and ferromagnetism.

Raman scattering work on $RuSr_2GdCu_2O_8$ and related materials[9–16] has uncovered several anomalous spectral features. Notably, a broad excitation around 140 cm^{-1} appears upon cooling below T_M,[9,10,12,15] but both the Raman selection rules and the mode energy are difficult to reconcile with an interpretation in terms of magnetic excitations. Further, pronounced phonon anomalies were observed at T_M.[12] In particular, a mode at ~ 260 cm^{-1} corresponding to rotations of the RuO_6 octahedra around the c axis[16] splits into two distinct modes below T_M. While standard spin-phonon coupling mechanisms can explain the frequency shifts of other modes at T_M, the splitting of the 260 cm^{-1} mode indicates a lowering of the lattice symmetry associated with the onset of magnetic order.

In an effort to contribute to an understanding of the anomalous Raman spectra of $RuSr_2GdCu_2O_8$, we have carried out a Raman scattering study of samples in which divalent Sr ions were partially replaced by trivalent La ions, so that the density of mobile holes is systematically reduced. It was previously established[17,18] that the electrical conductivity decreases and superconductivity disappears with increasing La content, whereas the magnetic transition temperature increases. The same trends were observed when the charge density was modified by substitutions on the Gd site.[19] We find that the 140 cm^{-1} mode shifts to higher frequency with increasing La content, in concert with the increasing magnetic transition temperature. However, its spectral weight decreases rapidly as x increases. The anomaly of the 260 cm^{-1} vibration, on the other hand, evolves smoothly with x. We discuss these findings in terms of ordering of the spin, charge, and orbital degrees of freedom in the RuO_2 layers.

II. EXPERIMENTAL DETAILS

Five polycrystalline pellets of composition $Ru(Sr_{1-x}La_x)_2GdCu_2O_8$($x=0$, 0.01, 0.03, 0.05, and 0.10) were synthesized following a previously established protocol.[17,18] Figure 1 shows the magnetic susceptibility of these samples. The $x=0$ sample shows a superconducting transition at $T_c=40$ K. Superconductivity with $T_c=30$ K was also found for the $x=0.01$ sample, while the remaining samples are nonsuperconducting. The conductivity of the $x=0.1$ sample shows a semiconducting temperature dependence. The magnetic transition temperatures range from $T_M=140$ K for $x=0$ to 180 K for $x=0.1$. The data of Fig. 1 also show that the net magnetization below T_M decreases rapidly for $x>0.01$. These findings are consistent with those reported in Ref. 17.

The Raman scattering measurements were performed in back-scattering geometry with a DILOR triple-grating spectrometer using unpolarized light of wavelength 514.53 nm. The scattered light was collected with a back-illuminated Jobin Yvon Spectrum-One charge-coupled device (CCD) camera cooled with liquid nitrogen. The samples were mounted in a closed-cycle He cryostat.

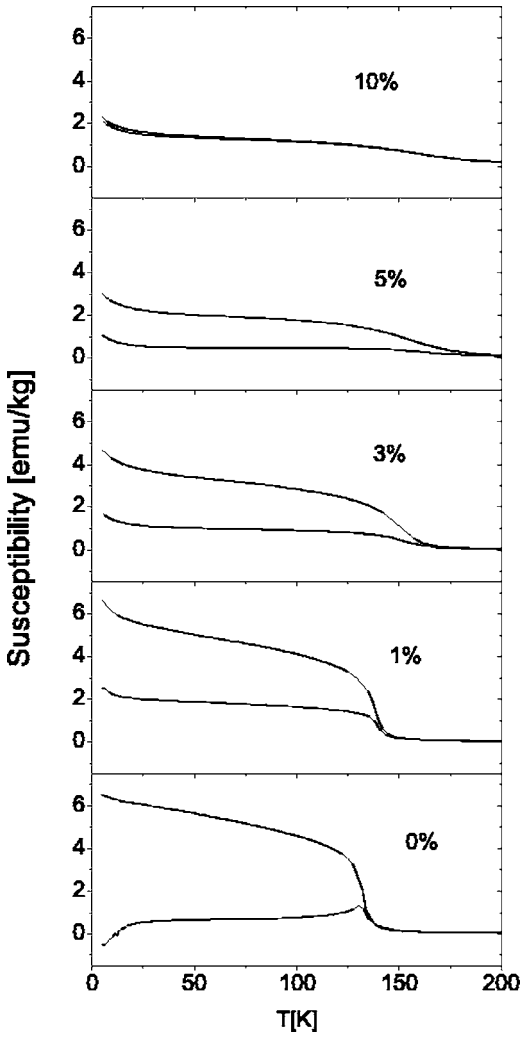

FIG. 1. Magnetic susceptibility of $Ru(Sr_{1-x}La_x)_2GdCu_2O_8$ in an applied field of 10 Oe. The La content is mentioned in the legend. Upper (lower) curves were taken in field-cooled (zero-field-cooled) mode.

III. RESULTS AND DISCUSSION

Figure 2 provides a synopsis of the evolution of the low-temperature Raman spectrum with La content. Apart from a gradual broadening of the phonon excitations, which is probably attributable to increased substitutional disorder, we have observed two specific trends.

First, the broad mode observed at 136 cm^{-1} in the La-free sample shifts to 145 cm^{-1} for $x=0.01$ (Fig. 3). This shift is in approximate proportion to the La-induced increase in T_M. At the same time, however, the mode also broadens considerably. The spectral weight of the mode decreases with increasing temperature and vanishes above T_M, in agreement with prior reports.[12] Despite the continuously increasing magnetic ordering temperature, it is no longer discernible for samples with $x \geq 0.03$. Second, the splitting of the 260 cm^{-1} oxygen vibration is gradually reduced with increasing La content, although the onset of this anomaly follows T_M within the experimental error (Fig. 4). Notably, the evolution of the mode below T_M is very similar in samples that are metallic and superconducting on the one hand, and semiconducting on the other hand. The anomalies of the other phonon modes that were previously reported are less pronounced, and a doping-dependent trend is difficult to discern.

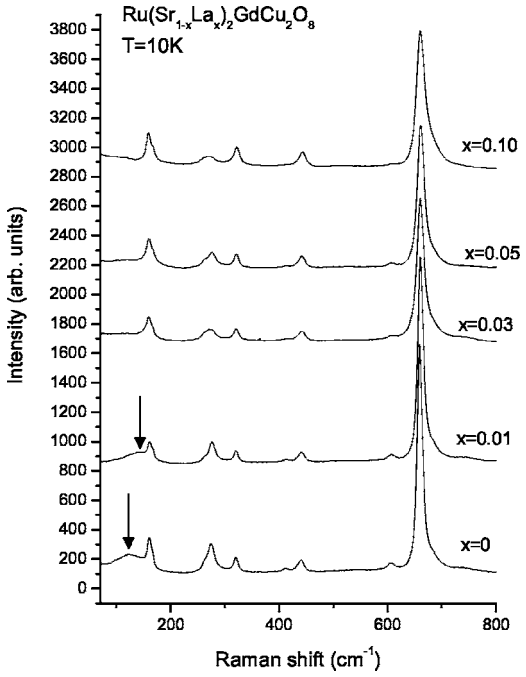

FIG. 2. Raman spectra of $Ru(Sr_{1-x}La_x)_2GdCu_2O_8$ at $T=10$ K. The spectra were offset vertically for clarity. The low-energy peak is marked with an arrow.

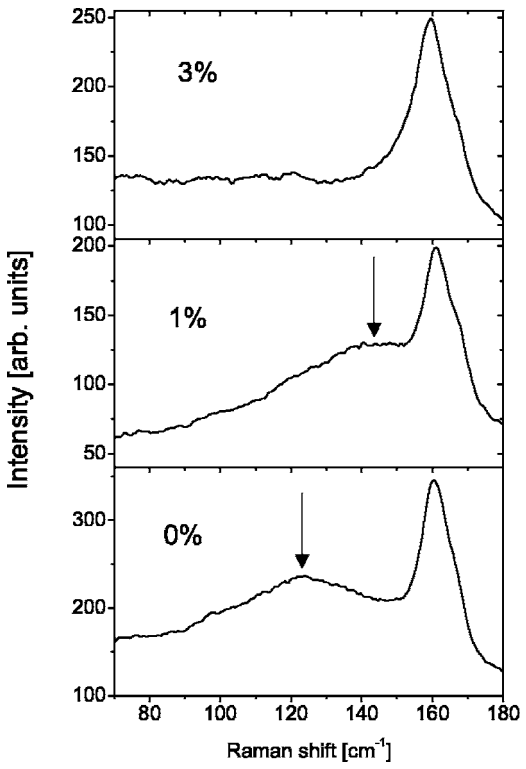

FIG. 3. Evolution of the low-energy Raman peak (marked with an arrow) with La content at $T=10$ K.

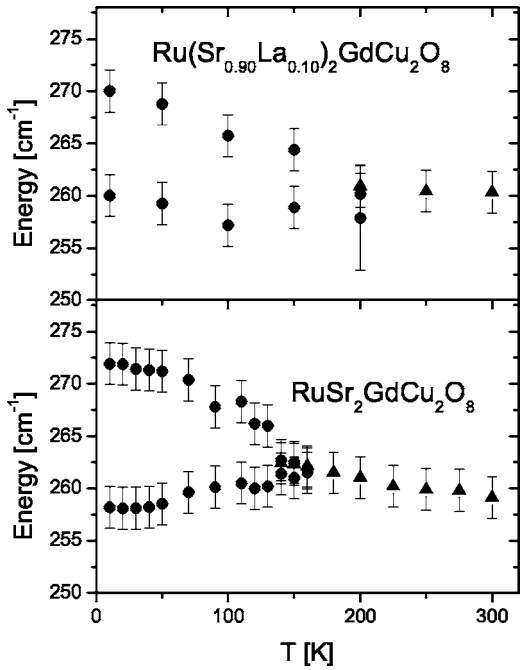

FIG. 4. Evolution of the 260 cm^{-1} phonon mode below the magnetic transition temperature for pure and 10% La-substituted $RuSr_2GdCu_2O_8$ (circles, peak fitted with two Voigt lines; triangles, peak fitted with one Voigt line).

We discuss these observations in terms of the RuO_2 subsystem, because the Cu ions contribute at most weakly to the magnetic order parameter. X-ray absorption spectroscopy shows[20] that La-free $RuSr_2GdCu_2O_8$ contains ruthenium ions in formal valence states +4 and +5 in roughly equal proportion. The small ordered moment below T_M indicates that Ru^{4+} is in the low-spin state and hence contains orbitally degenerate t_{2g} electrons. As evidence of orbital order has been reported in several other compounds containing Ru^{4+} ions,[21] coincident spin and orbital order is a natural origin of the lowering of the lattice symmetry indicated by the splitting of the 260 cm^{-1} mode below T_M. Similar phonon anomalies in Ca_2RuO_4 (Ref. 22) and $Ca_3Ru_2O_7$ (Ref. 23) were also interpreted as indications of orbital order. Direct evidence of a lattice superstructure attributable to orbital order has thus far not been reported for $RuSr_2GdCu_2O_8$. However, the coupling of t_{2g} electrons to the lattice is known to be much weaker than that in the more widely studied manganites containing valence electrons in bond-directional e_g orbitals, where lattice superstructures associated with orbital ordering are readily observable. In contrast, prior work on other systems with t_{2g} valence electrons has shown that the manifestations of orbital order in x-ray or neutron diffraction patterns are quite subtle. Single-crystal diffraction studies required to detect the corresponding superstructure reflections have thus far not been reported for $RuSr_2GdCu_2O_8$. Along the same lines, the weak lattice coupling and strong spin-orbit coupling of the Ru t_{2g} electrons may also explain why the onsets of spin and orbital order coincide in $Ru(Sr_{1-x}La_x)_2GdCu_2O_8$. Finally, if orbital order is at the root of the phonon anomalies at T_M, it is not surprising that vibrations of the oxygen ligands around the Ru ions are most strongly affected.

We next discuss our observations on the 140 cm^{-1} mode. While the parallel shift of T_M and the energy of this mode with La content seems superficially consistent with a magnon excitation, the unexpectedly strong evolution of its spectral weight underscores previous indications that the origin of this mode is more complex. A comparison with other materials with t_{2g} valence electrons is also useful in this context. Specifically, Raman scattering experiments on insulating pseudocubic titanates[24] and vanadates[25] have recently shown broad, low-energy excitations akin to that observed in $RuSr_2GdCu_2O_8$. These modes were interpreted as "orbitons," that is, coherent shape oscillations of the occupied t_{2g} orbitals. However, since modes of comparable energy have not been reported in other compounds with orbitally ordered Ru^{4+} ions, and because the electronic mode in $Ru(Sr_{1-x}La_x)_2GdCu_2O_8$ shows a rather different hole content dependence than the lattice anomaly that presumably reflects orbital order, the origin of this mode appears even more subtle. Metallic layered cobaltates of composition Na_yCoO_2 offer a more revealing comparison. Both Raman scattering[26] and infrared ellipsometry[27] work on these materials have recently provided evidence of electronic modes with energies comparable to that studied here. As the spectral weight and the energy of these modes is sensitive to the onset of magnetic order, they were discussed as magnetopolaron excitations comprising an intimate admixture of spin, charge, and orbital degrees of freedom.[27] Like the mode discussed here, the magnetopolaron modes were only observed over a narrow range of hole density in the CoO_2 layers. This was attributed to the narrow stability range of a state exhibiting spin, charge, and orbital order around a commensurate hole concentration $y=0.75$.

A similar scenario may provide an explanation of the unusual behavior of the 140 cm^{-1} mode. If the filling factor of the Ru t_{2g} orbitals in $Ru(Sr_{1-x}La_x)_2GdCu_2O_8$ with $x\sim 0$ is near 4.5 (which is consistent with x-ray absorption experiments), a commensurate charge-ordered state could be stabilized. The 140 cm^{-1} mode may then be a manifestation of this additional superstructure. Broad modes attributable to coherent charge-density oscillations were actually observed by Raman scattering in several materials undergoing charge-density-wave instabilities.[28] The possibility of charge and orbital ordering in $RuSr_2GdCu_2O_8$ has also been pointed out in recent theoretical work, but specific ordering patterns were not discussed.[29] The simplest charge-ordered state consistent with an average Ru valence of 4.5 would be a "checkerboard" comprising Ru^{4+} and Ru^{5+} sublattices. Because of the net different magnetic moments of both sublattices, such a state would be ferrimagnetic. In this context, it is interesting to observe that the ferromagnetic magnetization also exhibits a rapid drop with increasing x, as noted in Sec. II above. Both observations are hence consistent with a ferrimagnetic charge-ordered state that is rapidly disrupted as x increases. The residual ferrimagnetic magnetization for $x>0.01$ is then perhaps a consequence of residual charge order in a small volume fraction.

IV. CONCLUSIONS

In summary, we have monitored the evolution of the salient anomalous features in the Raman spectra of

$Ru(Sr_{1-x}La_x)_2GdCu_2O_8$ as a function of hole density. While the anomalous behavior of the 260 cm^{-1} oxygen vibration at the magnetic transition temperature depends smoothly on x, the broad mode around 140 cm^{-1} disappears rapidly for $x > 0.01$. In conjunction with the anomalous x dependence of the ferromagnetic magnetization, these observations can be understood if orbital order of the Ru^{4+} ions accompanies magnetic ordering over an extended range of doping levels, whereas an additional Ru^{4+}-Ru^{5+} charge-ordered state is only stable over a narrow range around $x=0$. While this scenario is consistent with currently available powder diffraction data, it remains speculative at this stage. Our results therefore call for a dedicated search for the corresponding superstructure reflections in single-crystal diffraction experiments.

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[1] L. Bauernfeind, W. Widder, and H. F. Braun, Physica C **254**, 151 (1995).
[2] O. Chmaissem, J. D. Jorgensen, H. Shaked, P. Dollar, and J. L. Tallon, Phys. Rev. B **61**, 6401 (2000).
[3] L. T. Yang, J. K. Liang, Q. L. Liu, C. Q. Jin, X. M. Feng, G. B. Song, J. Luo, F. S. Liu, and G. H. Rao, J. Solid State Chem. **177**, 1072 (2004).
[4] C. Bernhard, J. L. Tallon, Ch. Niedermayer, Th. Blasius, A. Golnik, E. Brucher, R. K. Kremer, D. R. Noakes, C. E. Stronach, and E. J. Ansaldo, Phys. Rev. B **59**, 14099 (1999).
[5] J. W. Lynn, B. Keimer, C. Ulrich, C. Bernhard, J. L. Tallon, Phys. Rev. B **61**, R14964 (2000).
[6] H. Takagiwa, J. Akimitsu, H. Kawano-Furukawa, and H. Yoshizawa, J. Phys. Soc. Jpn. **70**, 333 (2001).
[7] A. Butera, A. Fainstein, E. Winkler, and J. Tallon, Phys. Rev. B **63**, 054442 (2001).
[8] H. Aliaga and A. A. Aligia, Physica B **320**, 34 (2002).
[9] V. G. Hadjiev, C. Bernhard, C. T. Lin, T. Ruf, M. Cardona, and J. L. Tallon, Physica C **341-348**, 2255 (2000).
[10] V. G. Hadjiev, A. Fainstein, P. Etchegoin, H. J. Trodahl, C. Bernhard, M. Cardona, and J. L. Tallon, Phys. Status Solidi B **211**, R5 (1999).
[11] D. J. Pringle, J. L. Tallon, B. G. Walker, and H. J. Trodahl, Phys. Rev. B **59**, R11679 (1999).
[12] A. Fainstein, P. Etchegoin, H. J. Trodahl, and J. L. Tallon, Phys. Rev. B **61**, 15468 (2000).
[13] M. N. Iliev, A. P. Litvinchuk, V. N. Popov, R. L. Meng, L. M. Dezaneti, and C. W. Chu, Physica C **341-348**, 2209 (2000).
[14] A. Fainstein, C. A. Ramos, R. G. Pregliasco, A. Butera, H. J. Trodahl, G. V. M. Williams, and J. L. Tallon, Physica B **320**, 322 (2002).
[15] A. Fainstein, A. E. Pantoja, H. J. Trodahl, J. E. McCrone, J. R. Cooper, G. Gibson, Z. Barber, and J. L. Tallon, Phys. Rev. B **63**, 144505 (2001).
[16] V. G. Hadjiev, J. Backstrom, V. N. Popov, M. N. Iliev, R. L. Meng, Y. Y. Xue, and C. W. Chu, Phys. Rev. B **64**, 134304 (2001).
[17] P. Mandal, A. Hassen, J. Hemberger, A. Krimmel, and A. Loidl, Phys. Rev. B **65**, 144506 (2002).
[18] J. Hemberger, A. Hassen, A. Krimmel, P. Mandal, and A. Loidl, Physica B **312-313**, 805 (2002).
[19] P. W. Klamut, B. Dabrowski, J. Mais, and M. Maxwell, Physica C **350**, 24 (2001).
[20] R. S. Liu, L.-Y. Jang, H.-H. Hung, and J. L. Tallon, Phys. Rev. B **63**, 212507 (2001).
[21] See, e.g., I. Zegkinoglou, J. Strempfer, C. S. Nelson, J. P. Hill, J. Chakhalian, C. Bernhard, J. C. Lang, G. Srajer, H. Fukazawa, S. Nakatsuji, Y. Maeno, and B. Keimer, Phys. Rev. Lett. **95**, 136401 (2005); R. Mathieu, A. Asamitsu, Y. Kaneko, J. P. He, X. Z. Yu, R. Kumai, Y. Onose, N. Takeshita, T. Arima, H. Takagi, and Y. Tokura, Phys. Rev. B **72**, 092404 (2005); G. Cao, X. N. Lin, L. Balicas, S. Chikara, J. E. Crow, and J. P. Schlottmann, New J. Phys. **6**, 159 (2004); J. H. Jung, Z. Fang, J. P. He, Y. Kaneko, Y. Okimoto, and Y. Tokura, Phys. Rev. Lett. **91**, 056403 (2003); P. Khalifah, R. Osborn, Q. Huang, H. W. Zandbergen, R. Jin, Y. Liu, D. Mandrus, and R. J. Cava, Science **297**, 2237 (2002).
[22] H. Rho, S. L. Cooper, S. Nakatsuji, H. Fukazawa, and Y. Maeno, Phys. Rev. B **71**, 245121 (2005).
[23] M. N. Iliev, S. Jandl, V. N. Popov, A. P. Litvinchuk, J. Cmaidalka, R. L. Meng, and J. Meen, Phys. Rev. B **71**, 214305 (2005); J. F. Karpus, R. Gupta, H. Barath, S. L. Cooper, and G. Cao, Phys. Rev. Lett. **93**, 167205 (2004).
[24] C. Ulrich, A. Gossling, M. Gruninger, M. Guennou, H. Roth, M. Cwik, T. Lorenz, G. Khaliullin, and B. Keimer, cond-mat/0503106 (unpublished).
[25] S. Miyasaka, S. Onoda, Y. Okimoto, J. Fujioka, M. Iwana, N. Nagaosa, and Y. Tokura, Phys. Rev. Lett. **94**, 076405 (2005).
[26] P. Lemmens, K. Y. Choi, V. Gnezdilov, E. Ya. Sherman, D. P. Chen, C. T. Lin, F. C. Chou, and B. Keimer, Phys. Rev. Lett. **96**, 167204 (2006).
[27] C. Bernhard, A. V. Boris, N. N. Kovaleva, G. Khaliullin, A. V. Pimenov, L. Yu, D. P. Chen, C. T. Lin, and B. Keimer, Phys. Rev. Lett. **93**, 167003 (2004).
[28] See, e.g., C. S. Snow, J. F. Karpus, S. L. Cooper, T. E. Kidd, and T.-C. Chiang, Phys. Rev. Lett. **91**, 136402 (2003); J. C. Tsang, J. E. Smith Jr., and M. W. Shafer, *ibid.* **37**, 1407 (1976).
[29] A. A. Aligia and M. A. Gusmao, Phys. Rev. B **70**, 054403 (2004).