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Temperature-dependent local exchange splitting in $SrRuO_3$

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Optical and magneto-optical data from the perovskite itinerant ferromagnet $SrRuO_3$ are presented and compared to fully relativistic, local spin-density approximation band-structure calculations. We find that the basic features of the optical data are well described by the ferromagnetic band calculation. To test recent predictions that the ferromagnetic transition in $SrRuO_3$ is driven by long-wavelength longitudinal spin fluctuations, we track the temperature dependence of the $O(2p) \rightarrow Ru(4d)$ interband transition which we observe in the magneto-optic conductivity. The absence of significant changes in the energy of this transition suggests that the ferromagnetic order is destroyed largely through transverse, not longitudinal, fluctuations of the ferromagnetic moment. We discuss the implications of these observations for the electronic structure of the ruthenium perovskites. [S0163-1829(99)51134-X]

Itinerant ferromagnetism (FM) at finite temperatures has been a source of controversy for decades.[1] The fundamental problem rests in how to properly describe the electronic correlations in the paramagnetic state. Despite significant theoretical progress, it is fair to say that a general understanding of these correlations eludes us, and requires further empirical guidance. The pseudocubic perovskite $SrRuO_3$ now provides an important challenge for our current understanding, just as elemental nickel has done before it. In addition to several experimentally determined anomalies,[2–4] it has been argued on theoretical grounds that the ruthenium oxides generally should display anomalously large fluctuations of the on-site moment amplitude.[5] In this picture of the electronic structure, the transition to FM $SrRuO_3$ should be dominated by long-wavelength fluctuations of the moment amplitude, despite its large moment of $1.6\mu_B$. A recent theory utilizes these fluctuations to provide the pairing mechanism for superconductivity in Sr_2RuO_4,[6] and support for this view has recently been provided by the strong enhancement of the spin-lattice relaxation rate in Sr_2RuO_4 at low temperatures.[7] In this work, we present experimental and band theoretical results on the optical and magneto-optical spectroscopy of $SrRuO_3$ and show that they compare favorably. Through an analysis of these results, we also provide spectroscopic evidence for the primacy of transverse moment fluctuations near T_C in $SrRuO_3$. Extensions to the band theory of FM require some degree of short-ranged order near and above T_C to explain our results.

For energetic reasons, longitudinal moment fluctuations are strongly peaked around $q=0$, so if they are important in $SrRuO_3$, the average exchange splitting should appear to decrease as T_C is approached from below. In turn, optical properties which are sensitive to the exchange splitting will be strongly temperature dependent.[5] From optical and magneto-optical (MO) measurements on $SrRuO_3$, we assign the $O(2p) \rightarrow Ru(4d)$ interband transition, and use this to monitor the magnetic exchange splitting as T_C is approached. We find that $SrRuO_3$ behaves as other, conventional large-moment ferromagnets, in that the band energies exhibit little dependence on the ferromagnetic transition.

Experimentally, we have determined the full conductivity tensor of $SrRuO_3$ over the visible range, using direct methods which do not require Kramers-Kronig transformation. Using spectroscopic ellipsometry at several incident angles, we determined the frequency-dependent conductivity at room temperature of a 1250 Å film of $SrRuO_3$ deposited by coevaporation on a $SrTiO_3$ substrate.[8] The real and imaginary parts of the optical conductivity $\sigma_{xx}(\omega)$ are shown in Fig. 1, in the frequency range between 0.67 and 4.5 eV. These plots were derived using a semi-infinite smooth slab

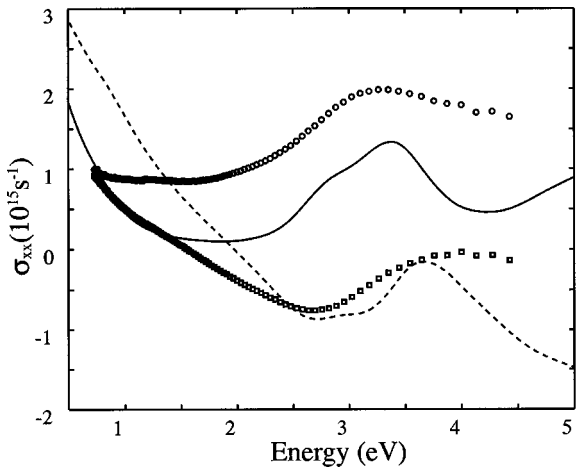

FIG. 1. Optical conductivity of $SrRuO_3$ at room temperature. Symbols are as follows: ''○'' σ_{1xx} (experiment); ''—'' σ_{1xx} (theory); ''□'' σ_{2xx} (experiment); ''- - -'' σ_{2xx} (theory).

model for the sample, for which we estimate systematic errors of less than 10% over the range covered. To determine $\sigma_{xy}(\omega)$, we measured both the Faraday rotation and ellipticity at several temperatures below the Curie point. For these transmission measurements, we used a 500 Å $SrRuO_3$ thin film deposited by laser ablation on MgO with a 1000 Å buffer layer of $SrTiO_3$, to avoid the background associated with thick $SrTiO_3$ substrates. Using measurements of $\theta_F(\omega)$ and $\epsilon_F(\omega)$ at 65 K, and room temperature ellipsometric measurements of $\sigma_{xx}(\omega)$, we calculated $\sigma_{xy}(\omega)$. The results of this calculation, scaled by the known temperature-dependent magnetization to indicate the expected zero-temperature behavior,[3] are shown in Fig. 2. These results are dominated by $\theta_F(\omega)$ and $\epsilon_F(\omega)$ and are largely insensitive to the details of the $\sigma_{xx}(\omega)$ measurement, even for large changes.

Together with the experimental data, we show results from fully relativistic band structure calculations in the local spin density approximation (LSDA), computed for the cubic structure.[9,10] The bands are shown in Fig. 3. This calculation gives a ground state moment of $1.56\mu_B$, which is very close

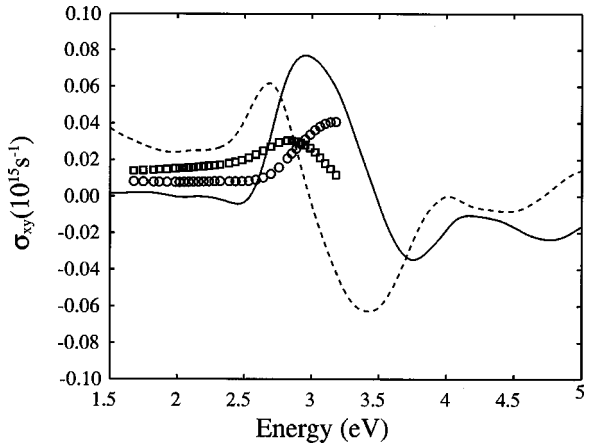

FIG. 2. Magneto-optic conductivity of $SrRuO_3$. Experimental points are calculated from the measured Faraday rotation and ellipticity of a 500 Å film of $SrRuO_3$ and the data shown in Fig. 1. Symbols are as follows: ''□'' σ_{1xy} (experiment); ''- - -'' σ_{1xy} (theory); ''○'' σ_{2xy} (experiment); ''—'' σ_{2xy} (theory).

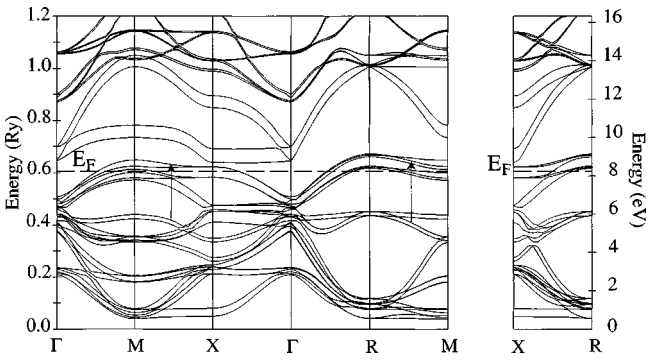

FIG. 3. Calculated band structure for $SrRuO_3$. Arrows indicate optical transitions discussed in the text.

to the measured value of $1.6\mu_B$,[3] and the exchange splitting of 0.55 eV is consistent with other calculations.[11,12] We have accounted for intraband contributions to the conductivity with a single Drude peak for σ_{xx} and with the conventional form for σ_{xy}, due to spin-orbit coupling.[13] As observed previously,[4] σ_{xx} at low frequency is significantly larger than that expected from the Drude form. Additionally, we find the low-frequency value of σ_{2xy} to be approximately five times greater than our conventional estimate, indicating that this excess conductivity is magneto-optically active. The origin of this excess conductivity is not understood presently.

The most obvious feature in the experimental data, which is reproduced in the calculation with reasonable accuracy, is the feature at ~3.2 eV in both the diagonal and off-diagonal conductivity. These peaks indicate the existence of a MO-active interband transition at this energy, and our calculations indicate that this peak is largely due to transitions of minority spin from the top of the oxygen *p*-like complex (0–0.45 Ry) to the top of the Ru($4d$) t_{2g}-like complex (0.45–0.65 Ry). Two representative transitions are indicated by arrows in Fig. 3. Transitions between the t_{2g} and e_g complexes are expected to be much weaker than the observed transition strength, due to the parity selection rule. The final states of these transitions form part of a narrow peak in the density of states (DOS) near the Fermi level, and drive the system to FM in the Stoner model.[11] Recent optical measurements have assigned this transition to the Mott-Hubbard gap, and assumed that the charge-transfer transitions occur at much higher-energies.[14] The detailed agreement between theory and experiment for our alternative assignment casts considerable doubt on the validity of this interpretation, and the conclusions which depend on it.

The mere existence of a MO-active transition allows us to conclude that at least one of the two states involved in the transition is magnetic. Moreover, magnetism is accompanied by spin-dependent wave functions and energy states, so that both the optical matrix elements and the energy differences between occupied and unoccupied states may contribute to σ_{xy}. Roughly speaking, $\sigma_{xy} \sim \sigma_{xx\uparrow} - \sigma_{xx\downarrow}$, so energy differences between time-reversed states will cause σ_{2xy} to be dispersive, or antisymmetric about the average transition energy, while matrix element differences will produce a symmetric, dissipative line shape.[15] The coincidence of the peak in σ_{1xx} and a dissipative peak in σ_{2xy} shows that the MO activity of the 3 eV transition is due to the spin-orbit perturbation of the matrix elements, coupled with spin asymmetry

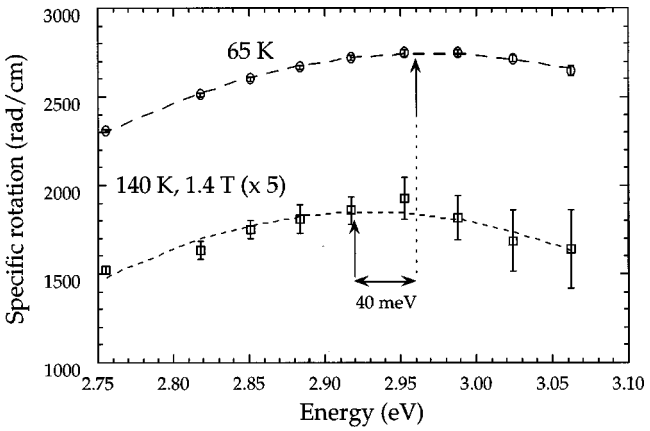

FIG. 4. The interband peak in the Faraday rotation at 65 and 140 K. The measurement at 140 K was done in a 1.4 T field, to ensure that the moment was along the optical axis. The high-temperature data are scaled up by a factor of 5.

in the ground-state occupation; this is the usual mechanism in ferromagnetic metals. This confirms our assignment of the final state to the t_{2g} complex, which exhibits strong spin-orbit mixing: we expect virtually no magneto-optic conductivity from e_g complex. Other than the magneto-optically inactive transitions to the e_g complex, our calculations indicate that no other optical transitions should lie within this energy range. The $O(2p) \rightarrow Ru(4d,t_{2g})$ transition is almost exclusively to a *minority* spin state, with little or no contribution to the conductivity from final states of majority spin. Thus the position of this MO active interband transition monitors the average energy splitting between the *p*-like and *d*-like bands of *a single spin species*, and consequently will be sensitive to the exchange splitting in these regions of the Brillouin zone.

The spin splitting of the bands is approximated well by a rigid band picture. Thus we expect that temperature-dependent shifts in the energy difference between spin-up and spin-down bands will be reflected as an absolute shift of the 3.2 eV interband transition, since the spin splitting of the initial *p*-like states is much weaker than the final *d*-like states. We have verified this by simulating the optical and MO conductivity of $SrRuO_3$ for a weakly magnetized state, by adding a 10 meV spin-dependent shift to the chemical potential of the nonmagnetic LSDA bands. In both the optical and MO conductivities, we find that the interband transition peak energy shifts down by more than 400 meV. The conclusions presented here depend primarily on global changes to the bands from on-site Hund's rule exchange coupling, which we expect to be preserved in the actual, weakly orthorhombic structure.

We focus on the peak at 2.9 eV in the Faraday rotation, which is shown in Fig. 4 for two different temperatures. The lower curve, taken at 140 K, was taken in a 1.4 T field in order to ensure that the material remained uniformly magnetized. The substrate contribution to the Faraday rotation could be subtracted reliably. The high-temperature curve has been scaled up by a factor of five for easier comparison with the data taken at 65 K. Overall, the Faraday rotation at 65 K is roughly a factor of 6 greater than that at 140 K. The dashed lines indicate parabolic fits to the data over the range shown, which provides our measure of the peak position.

As indicated in the figure, we observe a shift of only 40 meV, and in the absence of magnetism we can expect at least 30 meV of this to be the result of phonon effects.[16] If we assume $\Delta E \propto M^2$,[6] we should expect a change in Δ of 260 meV, and a shift in the interband transition of the same order. In nickel, vertex corrections are thought to reduce the measured exchange splitting by a factor of 2. If we assume that these are not significantly different in this material, this will reduce the expected shift to 130 meV, which is still more than three times the total experimental shift, and 13 times larger than our estimated magnetic contribution. Such strong disagreement leads us to conclude that $SrRuO_3$ loses its magnetic order by orientational disorder, with local moments persisting above T_C. We would expect paramagnetic $CaRuO_3$ to behave similarly, indicating that extrapolations from paramagnetic band calculations for this material should be treated with caution. A similar caveat should hold for the layered ruthenium oxides, in particular superconducting Sr_2RuO_4, though here the effects of lower dimensionality and large spin-orbit coupling must be taken into account.

Slater argued that local moments could persist above the transition temperature because of the relative insensitivity of band-structure calculations to the orientation of individual moments,[17] and modern extensions to band theory attempt to account for this.[1,18–20] In some magnetic materials, however, Slater's argument does not hold, notably in Ni metal and in $SrRuO_3$: band calculations of these materials display a strong sensitivity to spin alignment, so much so that the antiferromagnetic state is unstable to paramagnetism in the LSDA.[5,20] While the extensions to band theory have attempted to treat this problem through a combination of short-range order and moment amplitude fluctuations, they generically predict overly large moments above T_C,[19–21] and the support provided by neutron data for short-range order has been controversial.[1,22,23] To date, research on the validity of the extended band theory has been almost exclusively limited to nickel and iron; our results indicate that $SrRuO_3$ presents a rare and valuable addition to the class of materials in which this theory may be tested quantitatively.

Several features of our LSDA calculations suggest that $SrRuO_3$ may also be relevant to recent work on itinerant ferromagnetism in extended Hubbard models. While this field is still under development, our calculations exhibit features which appear necessary to stabilize FM in extended Hubbard models within the dynamical mean-field theory: flat, degenerate bands, with a strongly asymmetric DOS peaked near the band edge.[11,24,25] This theoretical approach to $SrRuO_3$ is especially interesting in light of the narrow t_{2g} bandwidth found in our calculation and others, which supports a localized point of view. For example, our calculated exchange splitting in $SrRuO_3$ is more than half its second-moment bandwidth, indicating strong coupling between the transverse moment fluctuations and the electron hopping.

From a phenomenological point of view, the zero-temperature moment inferred from the Curie constant above T_C is $2\mu_B$ ($\mu_{eff}=2.8\mu_B$), and the actual zero-temperature remanent moment is $1.6\mu_B$, so the Rhodes-Wohlfarth ratio between high- and low-temperature moments is 1.25;[26] with a T_C near 150 K, this puts $SrRuO_3$ very close to the *local moment* limit, near Gd and EuO. The magnetic states of these materials are characterized by relatively strong on-site

Coulomb repulsion U, which suppresses charge fluctuations and produces multiplet structures which are not naturally incorporated in the LSDA. The effective U for ruthenium may be estimated from atomic optical spectroscopy to be ~ 3 eV, and this value, together with the Ru^{3+} charge state given by the band theory (see also Ref. 5), gives the correct bare Ru level energy for an accurate tight-binding model.[27] Further detailed theoretical investigation, using both the dynamical mean field and the density-functional approaches, may thus help to establish some range of applicability for each model.

In summary, we have presented optical evidence that the transition to FM in $SrRuO_3$ is dominated by transverse fluctuations of robust local moments, in disagreement with recent predictions and in contrast with the spin-lattice relaxation rate measurements on the related material, Sr_2RuO_4. Within the current formulation of band theory of FM at finite temperatures, our result would imply that $SrRuO_3$ exhibits short-ranged magnetic order above the Curie point, but we have noted objections to the validity of this formulation. Experimental tests for such order, together with more focused theoretical study of this material, will clarify our general understanding of itinerant ferromagnetism.

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[1] T. Moriya, *Spin Fluctuations in Itinerant Electron Magnetism* (Springer-Verlag, Berlin, 1985).

[2] L. Klein *et al.*, Phys. Rev. Lett. **77**, 2774 (1996).

[3] L. Klein *et al.*, J. Phys.: Condens. Matter **9**, 10 111 (1996).

[4] P. Kostic *et al.*, Phys. Rev. Lett. **81**, 2498 (1998).

[5] I. I. Mazin and D. J. Singh, Phys. Rev. B **56**, 2556 (1997).

[6] I. I. Mazin and D. J. Singh, Phys. Rev. Lett. **79**, 733 (1997).

[7] T. Imai *et al.*, Phys. Rev. Lett. **81**, 3006 (1998).

[8] C. H. S. Ahn, Ph.D. thesis, Stanford University, 1996.

[9] Yu. A. Uspenskii *et al.*, Phys. Rev. B **54**, 474 (1996).

[10] E. T. Kulatov *et al.*, J. Magn. Magn. Mater. **163**, 331 (1996).

[11] D. J. Singh, J. Appl. Phys. **79**, 4818 (1996).

[12] P. B. Allen *et al.*, Phys. Rev. B **53**, 4393 (1996).

[13] J. L. Erskine and E. A. Stern, Phys. Rev. B **8**, 1239 (1973). Parameters are $\omega_p = 3.6$ eV, $\gamma = 2.5 \times 10^{13}$ s^{-1}, $v_F \approx 10^7$ cm/s, and a spin-orbit induced dipole moment $|P_0| = 0.21$ e Å.

[14] J. S. Ahn *et al.*, Phys. Rev. Lett. **82**, 5321 (1999).

[15] W. Reim and J. Schoenes, in *Ferromagnetic Materials*, edited by K. H. J. Buschow and E. P. Wohlfarth (Elsevier, Amsterdam, 1990), Vol. 5.

[16] B. Chakraborty and P. B. Allen, Phys. Rev. B **18**, 5225 (1978).

[17] J. C. Slater, *The Self-consistent Field for Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. 4.

[18] V. Korenman *et al.*, Phys. Rev. B **16**, 4032 (1977).

[19] J. B. Staunton and B. L. Gyorffy, Phys. Rev. Lett. **69**, 371 (1992).

[20] M. Uhl and J. Kübler, Phys. Rev. Lett. **77**, 334 (1996).

[21] B. S. Shastry, D. M. Edwards, and A. P. Young, J. Phys. C **14**, L665 (1981).

[22] H. A. Mook and J. W. Lynn, Phys. Rev. Lett. **57**, 150 (1986).

[23] G. Shirane, P. Böni, and J. L. Martínez, Phys. Rev. B **36**, 881 (1987).

[24] D. Vollhardt *et al.*, Z. Phys. B **103**, 283 (1997).

[25] J. Wahle *et al.*, Phys. Rev. B **58**, 12 749 (1998).

[26] P. R. Rhodes and E. P. Wohlfarth, Proc. R. Soc. **273**, 247 (1963).

[27] S. Froyen, Phys. Rev. B **22**, 3119 (1980).