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A search for magnetic resonance of ruthenium in octahedral coordination with oxygen

H.A. Blackstead [a,*], W.B. Yelon [b], M. Kornecki [a], M.P. Smylie [a], P.J. McGinn [c], Q. Cai [d], B.W. Benapfl [a], S.D. Knust [a]

[a] Physics Department, University of Notre Dame, Notre Dame, IN 46556, USA
[b] Materials Research Center and Department of Chemistry, Missouri University of Science and Technology, Rolla, MO 65409, USA
[c] Chemical and Biochemical Engineering Department, University of Notre Dame, Notre Dame, IN 46556, USA
[d] Department of Physics, University of Missouri, Columbia, MO 65211, USA

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ABSTRACT

We have searched, without success, for microwave-frequency magnetic resonance of Ru^{4+} and Ru^{5+} ions in a number of materials for which the Ru are in octahedral coordination with six oxygen. A number of ruthenates including RuO_2, $SrRuO_3$, $Sr_3Ru_2O_7$, $Ba_3Ru_2NiO_9$, Ba_2GdRuO_6, Sr_2YRuO_6, and Ba_2YRuO_6, which include paramagnetic, antiferromagnetic, and ferromagnetic spin configurations, have been examined. We present analysis which shows that the last material provides an optimized opportunity to detect antiferromagnetic Ru resonance for temperatures less than $T_N = 39\,K$; none is detected for frequencies as high as 35 GHz in magnetic fields up to $\mu_o H = 2\,T$. This result indicates that the antiferromagnetic magnon energy gap exceeds the energy associated with the signal frequency. $SrRuO_3$ is a known ferromagnetic contaminant phase in the rutheno-cuprates. We report neutron diffraction measurements on $SrRuO_3$, finding it to have an appreciable local moment at low temperatures, $1.25(0.1)\mu_B$; this moment vanishes near 165 K. We show that it also fails to exhibit ferromagnetic resonance, at least in the range 10–35 GHz. As a result of the diffraction and resonance studies, it is concluded that the reports of ferromagnetic resonance in superconducting rutheno-cuprates are actually due to antiferromagnetically ordered Cu in these materials, and the presence of even a few percent of $SrRuO_3$ as a potential contaminant is of little importance.

1. Introduction

Several materials of current interest contain magnetically ordered Ru; these include ferromagnets, antiferromagnets, and magnetic superconductors [1–9]. The rutheno-cuprates $GdSr_2Cu_2RuO_8$ (Gd-O8) and $Gd_{1.5}Ce_{0.5}Sr_2Cu_2RuO_{10}$ (Gd-O10) are widely believed to be ferromagnetic superconductors manifested by the anomalous (positive) magnetizations exhibited in field-cooled (FC) (but not zero-field-cooled (ZFC)) magnetization measurements. We will refer to this effect as "apparent ferromagnetism". For these systems, the magnetism can be examined by local probes such as neutron diffraction (ND), muon spin rotation, (μ^+SR), nuclear magnetic resonance (NMR), Mössbauer effect (ME), and microwave-frequency magnetic resonance (MR). Each of these local probes may provide information contributing to the understanding of high-temperature superconductivity (HTSC), an effect which continues to defy theorists more than twenty years post discovery. The supercon ducting rutheno-cuprates, through the Ru and Cu magnetism, provide another independent "window" to probe this phenomenon. The feature added to the physics of several of these Ru-bearing materials is the co-existence of magnetism with superconductivity at a high temperature, a synergism long thought unlikely.

Early microwave-frequency magnetic resonance experiments [10] found what appeared to be a ferromagnetic resonance in Gd-O8. These results have been reinforced by the results of several nuclear magnetic resonance experiments [11–17] on Gd-O8 which have been interpreted to indicate that the Ru moments are ferromagnetically aligned in the basal plane. Liu [18] et al. carried out near-edge X-ray absorption measurements and suggested that the Ru ions are mixed valent with ferrimagnetic order. These data are at odds with extensive neutron diffraction [19,20] studies which find that in Gd-O8 the Ru moments are antiferromagnetic along the *c*-axis, with stringent limits on any possible weak-ferromagnetic Ru component.

For the homologue $^{153}Eu_{1.5}Ce_{0.5}Sr_2Cu_2RuO_{10}$ (Eu-O10) the neutron diffraction results are in even greater contrast [21], finding no antiferromagnetic order for the Ru moments, while

* Corresponding author.
E-mail address: blackstd@nd.edu (H.A. Blackstead).

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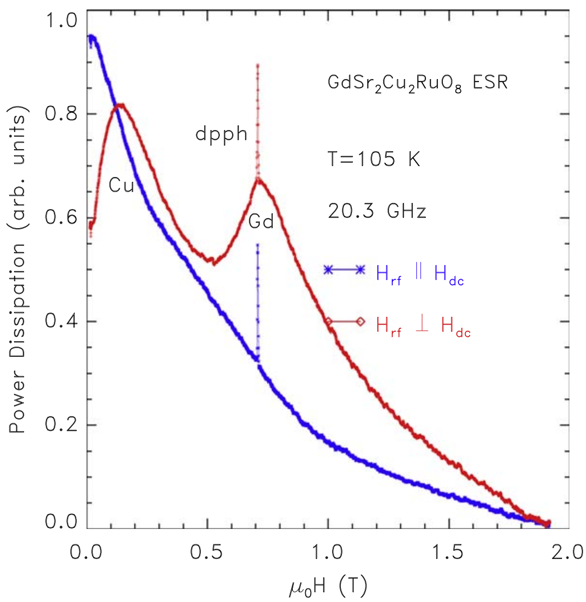

Fig. 1. Resonance data for a sample of $GdSr_2Cu_2RuO_8$ at $T = 105$K at a frequency of 20.3 GHz. The data are with $H_{rf} \| H_{dc}$, and also with $H_{rf} \perp H_{dc}$. These data show that two modes are excited. In ferromagnets, one resonance mode only can be excited with $H_{rf} \perp H_{dc}$, while in antiferromagnets, two modes may be excited. The Gd ESR is superimposed on the Cu AFMR modes which are characteristically broad, a consequence of a short Cu spin–spin relaxation time. The Cu signal intensity is ~4.4 times larger than that of the *dpph*.

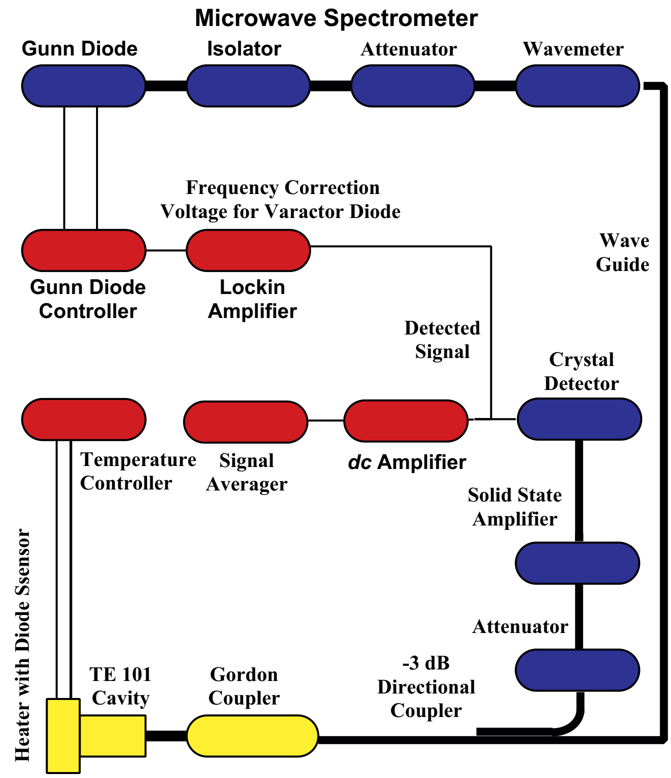

Fig. 2. *K*-band (20.3 GHz) microwave spectrometer block diagram. A Gordon coupler is used to optimize the impedance match of the resonant cavity to the waveguide. The solid-state amplifier has a gain of ~25 db, enabling low- power (~1 mw) excitation of the sample. The temperature of the cavity is maintained with a stability of approximately 10 mK using a combination of diode and capacitor temperature sensors.

polarized neutron studies excluded any Ru ferromagnetism. The O10 materials also exhibit the same magnetic and resonance phenomena as seen in the O8's. There is evidence for 2-d antiferromagnetic Ru order at a transition temperature significantly higher than is associated with the magnetization anomaly [22].

In Fig. 1, MR data on a superconducting sample of Gd-O8 are given for two *rf–dc* field configurations. These data show (in addition to the paramagnetic Gd ESR signal) that two resonance modes are excited, establishing that the magnetic sublattice which exhibits this behavior is not ferromagnetic. In the case of $H_{rf} \| H_{dc}$, selection rules permit the excitation of antiferromagnetic (or weak ferromagnetic) modes, while with $H_{rf} \perp H_{dc}$, paramagnetic, ferrimagnetic, ferromagnetic, and antiferromagnetic (or weak ferromagnetic) modes may be excited. These modes are observed until they are overwhelmed by superconducting fluxon dissipation at lower temperatures. In the following, we show that this is not due to the Ru sublattice, or to $SrRuO_3$, a potential ferromagnetic contaminant. By elimination (and in comparison to other materials which have Cu but no Ru), the Cu sublattice is the only possible source of these resonant modes [23]. These modes are very broad, with line-widths in excess of $\mu_0 H = 2$ T. There is substantial reluctance to accept a material with magnetically ordered cuprate planes as being a superconductor. Since this is an issue of consequence to potential theories of superconductivity, we have carried out a series of experiments designed to probe the origin and nature of the magnetic resonances in ruthenates and the excited (magnon) states of the magnetic system.

2. Microwave spectrometers

We used several different microwave spectrometers operating in "X", "Ku", "K", and "R" bands; with minor differences, all of these follow the block diagram illustrated in Fig. 2. Each of these spectrometers utilizes a microwave cavity operating in the TE_{101} mode, with the sample mounted in the center of the cavity bottom, where H_{rf}, the *rf* magnetic field (as much as ~0.5 Oe), is nearly uniform [24]. In the case of the 35 GHz system, a cylindrical TE_{011} cavity has also been employed. The steady field, H_{dc}, applied in the plane of the cavity bottom, was varied from 0–1.9 T. This field can be rotated relative to the direction of H_{rf}, permitting the detection of both modes which an antiferromagnetic material may exhibit. The feature which makes this spectrometer design nearly unique is that it does not utilize modulation of the steady field; the reflected signal is directly detected. Thus, the signals produced are proportional to the *rf* power dissipated in the sample, not its field derivative. A −3 db directional coupler is used to separate the signal reflected from the cavity from the input power. A low-noise solid-state microwave amplifier with a gain of 25–30 db is used to amplify the signal reflected from the cavity before detection. A sensitive *dc* amplifier, which includes a stable offset circuit, is used to amplify the *dc* signal detected by the point contact diode. In operation, the Gunn diode frequency is modulated at 10 kHz with a sine-wave applied to a varactor diode in the Gunn cavity. The resulting *ac* signal is detected with a lock-in amplifier connected to the output of the point contact diode detector. The modulated signal amplitude and its phase are used in a feedback circuit to "lock" the Gunn diode frequency to that of the resonant frequency of the cavity. Thus, the Gunn diode frequency "tracks" field-induced changes in the resonant frequency of the cavity. As a result, this spectrometer is sensitive only to "χ" (the loss component of the complex susceptibility). A digital signal averager is used to collect and average the field-dependent data.

These spectrometers are very sensitive, especially for resonances with large line-widths. In Fig. 3, a sensitivity calibration signal obtained using our 20.3 GHz system and a sample