

Condensed Matter

Electron Spin Resonance with Far Infrared Light

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The electron spin resonance (ESR) method is a well-established technique, extensively used in physics, chemistry and biology. Traditional ESR is done in a resonant cavity at microwave frequencies. The use of a high Q cavity provides great sensitivity, but it also places an upper limit on the frequency range: for wavelengths of less than 1cm, the size of the cavity becomes inconveniently small to handle. As long as the iron-bore technology placed an upper limit on the magnetic field as well, an easy compromise was found. As a result, most of the ESR measurements are still done at frequencies below 30GHz, and at fields less than 1Tesla.

The advent of inexpensive superconducting magnets changed this situation. High field ESR was explored by a number of research groups, in the US [1] and elsewhere [2-4]. The highest fields have been achieved at the National High Magnetic Field Laboratory [1]. The layered superconductor Sr_2RuO_4 , and molecular magnets like Fe_8 have been studied [5,6]. High resolution / high field techniques were applied to biological systems at Cornell University [7]. Electron spin resonance studies on fullerenes are conducted at the University of Pennsylvania [8]. Although in a typical high field ESR measurement no resonant cavity is employed, one aspect of the traditional ESR survived in all of the efforts listed above: the use of a fixed frequency, narrow band source, typically a Gunn diode or an IR laser.

The new instrumentation, installed at the NSLS U12IR beamline, breaks with this tradition. We use the intense, broad-band, far infrared radiation from the synchrotron source. An FT IR (Fourier Transform Infrared) spectrometer provides frequency selectivity. The result is a flexible device that is not restricted to the frequencies represented by the sources: a device that is able to map the full frequency - magnetic field (f - H) plane in search of absorption features. The frequency range extends continuously from the microwaves and millimeter waves to the infrared, and it includes

- the free electron spin resonance frequency ($\omega_0 = 15\text{cm}^{-1}$ in $H = 16\text{T}$)
- the AF resonance frequency (on a typical model system, $\text{NiF}_2, \omega_0 = 31\text{cm}^{-1}$)
- the energy of thermal excitations ($\omega = 70\text{cm}^{-1}$ at $T = 100\text{K}$)
- the interaction energy of many interesting electron systems ($\omega = 8.07\text{cm}^{-1}$ at $E = 1\text{meV}$)

The price paid for having the broad frequency coverage is that our instrument has a frequency resolution that is much less than that of the fixed-frequency methods. Accordingly, the best samples for this spectrometer should have large and unknown internal fields and (relatively) broad resonance features. There is no shortage of such materials; in the most interesting systems the electrons are involved with so many interactions, that the ESR signal is in fact *too broad* for the traditional techniques. In particular, two of the exciting challenges in the theory of interacting electron systems, high temperature superconductivity and colossal magnetoresistance, are recognized to share a common thread: closely related antiferromagnetic compounds exist in both cases. The spectrometer is expected to be particularly useful for the study of these systems, in the *undoped* antiferromagnetic and in the *weakly doped* regime.

The energy and magnetic field range of our facilities will allow us to look at other aspects of the electronic response as well. Following the traditions of quantitative far-IR spectroscopy, we can explore the low energy excitation spectrum of the electrons. We can directly investigate the influence of magnetic fields on the optical conductivity, possibly uncovering unusual charge carrying collective electron states, gaps and pseudo-gaps, transport relaxation times and scattering processes. The low frequency part of our frequency domain overlaps with the frequencies investigated by the so-called "time resolved terahertz spectroscopy", also done in a magnetic field at UC-Berkeley [9,10].

The main components of the instrument are the high resolution Fourier transform IR spectrometer and the superconducting magnet (see Figure 1). The spectrometer (model SPS 200, made by Sciencetech) has two important features, the 100mm diameter of the optics, and the 400mm path length of the moving mirror. The large size of the optics allows for low frequency operations. The lower cut off frequency of the instrument is presently 2cm^{-1} , and further improvement is expected by fine-tuning the detector geometry. Notice that 2cm^{-1} corresponds to 60GHz, which is traditionally considered a "microwave" frequency. The long path length yields a high resolution, typically 0.01cm^{-1} (apodized). Combined with the brightness and power advantage of the synchrotron IR source, these features make the instrument quite unique for long wavelength applications. The SPS 200 operates under vacuum to avoid water vapor absorption and microphonism. The spectrometer has rooftop mirrors, and the primary mode of operation is with a fixed input polarizer, a 45° rotated polarizer beam-splitter, and a rotating polarizer chop-

per at the output. All polarizers are of large area grids, manufactured on mylar by a holographic process. The efficiency is close to 100% for all wavelengths up to the cutoff determined by the grid separation ($4\mu\text{m}$).

Oxford Instrument's 16T magnet has a vertical bore, and the light beam is parallel to the magnetic field. A set of three, wedged single crystal quartz windows at the bottom provide a large aperture optical access to the sample from below, along the vertical axis of the magnet. Alternatively, we can use light pipes, as indicated in Figure 1, to guide the infrared light to the sample. The variable temperature insert allows accurate regulation of the sample temperature between 1.2K and 300K (the lowest temperature depends on the actual measurement configuration). The sample space at the center of the magnet is 37mm wide, but some of this space may be taken up by the light focusing and sample support structures. The optimum sample is a disk of about 1cm in diameter and a few millimeters in thickness. For a sample of this size the magnetic field is homogenous within 10 gauss.

The material selected for our first spin resonance study was LaMnO_3 , a well-known antiferromagnet, and the parent compound of the so-called colossal magnetoresistance materials. In terms of an ionic limit, the Mn^{3+} has the electronic configuration of $t_{2g}^3 e_g^1$. The strong Hund's rule coupling causes the electron spins to form an $S=2$ state. The single electron on the two-fold degenerate e_g orbital causes a collective Jahn-Teller distortion, resulting in a lattice distortion of $c/\sqrt{2} < a, b$ in the Pbnm structure. The distortion selects one of the MnO_2 planes, where the Mn-O distances follow an alternating pattern of short and long bonds. The hybridization of the e_g^1 electron and the O orbitals results in a coupling between the Mn sites [11]. In the presence of "antiferromagnetic" orbital order the spin coupling is ferromagnetic (FM), leading to the alignment of the spins within each of the distorted planes. LaMnO_3 is still an antiferromagnet: In the direction perpendicular to the planes, the spin coupling remains antiferromagnetic, as expected in the absence of alternating orbital order. The magnetic structure is illustrated in Figure 2. The resonance linewidth of pure LaMnO_3 is too broad for traditional ESR and it was first detected at sub-mm wavelengths in a 21T field by Mitsudo and co-workers [2].

The measurements were done on an excellent oriented single crystal LaMnO_3 sample provided by Jianshi Zhu (University of Texas, Austin). In the low temperature Neel state spin resonance does not require the application of an external magnetic field. Figure 3 shows the results of the broad-band transmission measurements done at zero magnetic field, as a function of the temperature. The quasi-sinusoidal modulation of the background transmission is caused by interference

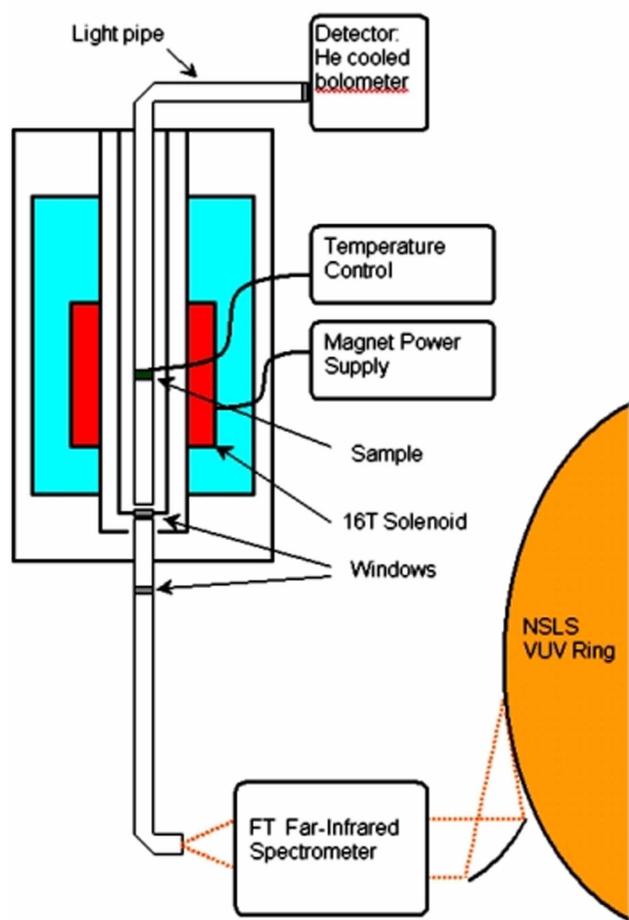


Figure 1. Schematic representation of the measurement configuration with light pipes.

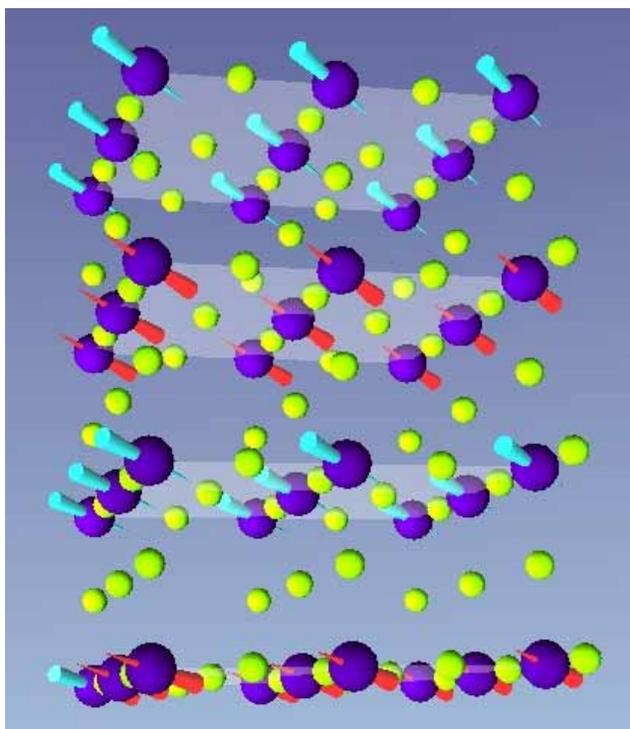


Figure 2. Structure of the LaMnO_3 . The red and blue arrows indicate the spin order.

between light reflected from the front and back surfaces of the sample, whereas the temperature dependent dip is due to the zero-field antiferromagnetic resonance. At low temperatures, the spin resonance frequency agrees well with the energy of the $k=0$ magnons, measured by neutron spectroscopy [12]. The fits to the data, shown in the right side panel, involve only one

temperature dependent parameter, the spin resonance frequency. It is somewhat surprising that the spin susceptibility is independent of the temperature within the experimental error. Moreover, in contrast to the theoretical expectations and experimental observations in simple AF systems, at the transition temperature the resonance frequency does not approach zero, but remains finite.

We studied the same sample in a magnetic field at two temperatures: in the antiferromagnetic state (4.2K) and in the paramagnetic state (200K). In this particular experimental set-up (depicted in Figure 1), the light from the synchrotron first passes through the spectrometer, the modulated output light of the spectrometer is brought to the sample, and the transmitted light is guided to the detector. The transmission spectrum was recorded at various magnetic fields, incremented in 1 Tesla steps. The result is a full, two-dimensional mapping of the spin resonance signal over the whole range of frequencies and magnetic fields, as shown in Figure 4. The total time required for recording a map was about 3 hours. In this first demonstration experiment, the set-up was far from being optimized, and significant improvements in the signal to noise ratio are expected.

The theory of the AF spin resonance has been developed in the early 50's by Keffer and Kittel [13], Nagamiya, and Yosida, and the experimental work was pioneered by Richards, Sievers and Tinkham. In the framework of a simple "mean field" approximation, the resonance frequency in zero external field is expressed as $\omega_0 \sim (\omega_E \omega_A)^{1/2}$, where ω_E and ω_A are frequencies corresponding to the exchange and anisotropy fields, respectively. Since the exchange energy can be either measured (by spectroscopy) or it can be estimated from

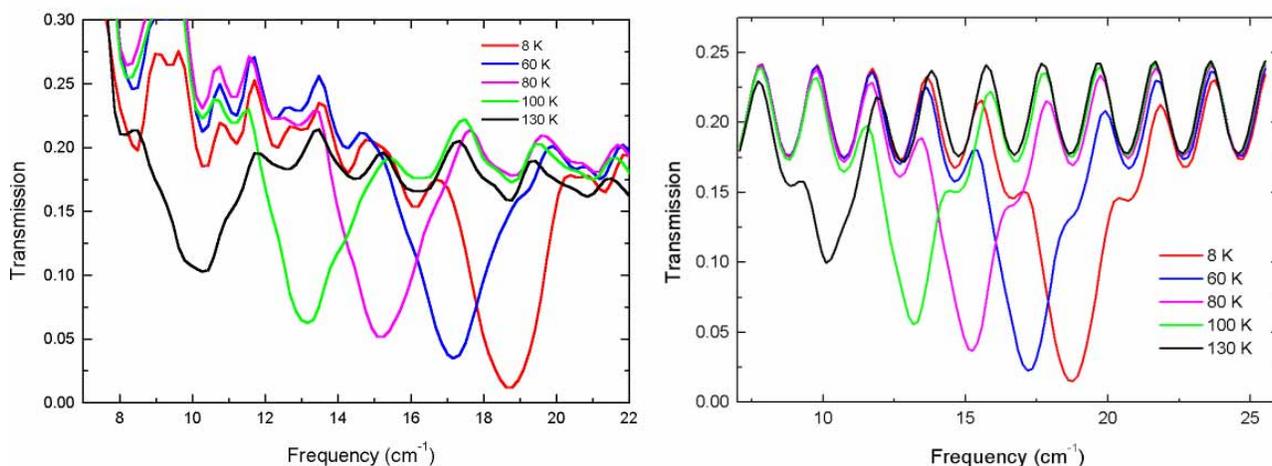


Figure 3. Left: Temperature dependence of the infrared transmission of LaMnO_3 . The dip in the transition is due to zero field AF spin resonance. Right: calculations using simple transmission theory and magnetic resonance formulae.

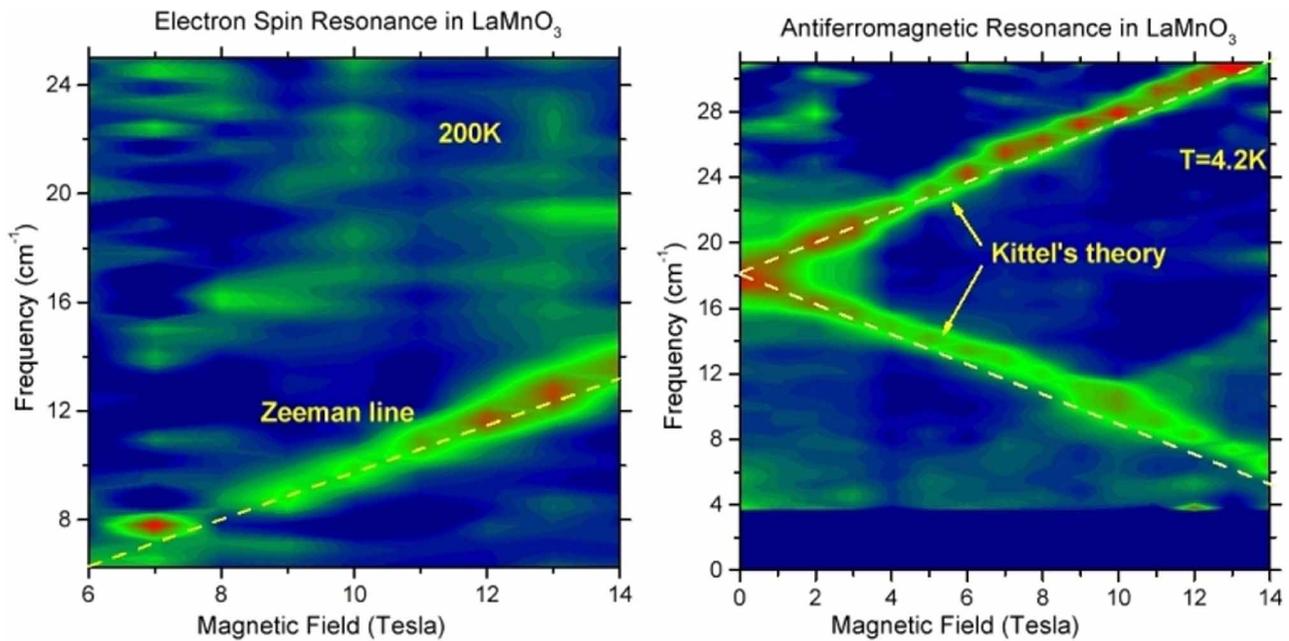


Figure 4. False-color representation of the spin resonance in the paramagnetic ($T=200\text{k}$) and antiferromagnetic ($T=4.2\text{K}$) state of LaMnO_3 . The lighter colors indicate enhanced absorption. The dashed lines correspond to the simplest fits to the data. These are the very first measurements performed on the new facility installed by the PI at the U12IR beamline of the NSLS.

the ordering temperature, the zero field AF resonance is one of the simplest and most effective ways to measure the microscopic *anisotropy energy*. The intensity of the resonance is a measure of the sublattice magnetization. Application of an external magnetic field causes a splitting of the left-rotating and right-rotating modes, as seen in the right panel of Fig. 4. Notice that the “fixed frequency” approach is entirely inadequate for zero field studies: it would be an unlikely coincidence if the internal parameters of the system yield a resonance frequency close to the experimental one.

The first measurements on the new spectrometer demonstrate the feasibility of doing ESR on the paramagnets and antiferromagnets in a non-resonant arrangement with a broad spectral coverage. The main reason for using the synchrotron source in these far-IR studies is the brightness and flux advantage over the conventional arc lamp [1]. Our spectrometer can be easily switched between internal and external sources, and one of the first tests we did was to compare the

performance in the two modes of operation. Depending on the frequency range and on the sample geometry, using the synchrotron results in a factor of 50 - 200 gain in the intensity. As long as the background noise is negligible the corresponding savings in measurement time is a factor of 7-14. However, in most of the measurements the background noise is an important contribution, and the use of the synchrotron light may very well bring the signal above the noise level, thereby turning a previously impossible measurement into a possible one.

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