Multifrequency electron spin resonance in strongly correlated metals and superconductors

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Contents

1. Introduction

The aim of the project was an electron spin resonance investigation of solids in which electron-electron correlations are of fundamental importance. Several systems were studied. The cuprate, organic and fullerene compounds investigated are metals, superconductors or magnetically ordered systems related to superconductivity in which electron correlations play an essential role. We measured and proposed a theory for the conduction electron spin life time in the inorganic superconductor, MgB_2. We completed work on the magnetic phase diagram of a cuprate system, Ca doped $YBa_2Cu_3O_6$, close to high temperature superconductivity. The mapping of the magnetic resonance modes of a layered organic weak ferromagnet, $ET_2Cu(N(CN)2)Cl$, solved a long standing problem of a material at the borderline of magnetic order and superconductivity. We showed, in collaboration with researchers at the University of Parma (Italy) and University of Cambridge (UK) that the fullerene compound, Li_4C_{60} is a crystalline superionic conductor with possible applications in electrical batteries. The recent progress of high frequency ESR spectrometers has renewed interest in the method. The high frequency ESR spectrometer at Budapest has been reconstructed, a new quasi optical bridge, a powerful mm-wave source, probe heads and a vibration free supporting structure were installed. As a result, the sensitivity was increased by more than an order of magnitude. Results were published in several articles in high impact scientific journals. Based on the work of the project, two PhD thesis were completed. The main goals of the project were fulfilled.

The original period was for 3 years from 1st February 2006 to 31st January 2009, the project was extended by 4 months until 31st May 2009. The extension served for writing publications and doing some ESR experiments.

2. Model systems investigated

2.1.Electron-hole doped cuprates

We investigated the electronic phase separation in lightly doped cuprates at the borderline of the antiferromagnetic and superconducting phases. This work is based on our discovery of an antiferromagnetic domain structure in $YBa_2Cu_3O_6$ that is highly sensitive to doping with electronic holes. The phase diagram of lightly hole doped cuprates has a remarkable complexity. A concentration of only 3% holes/Cu introduced into the CuO_2 planes of the two best studied cuprates, La_2CuO_4 and $YBa_2Cu_3O_6$, destroys the long range antiferromagnetic order of the Mott insulator parent compounds. A superconducting ground state is established at somewhat higher concentrations. There is growing experimental evidence for a spatial inhomogeneity in this transition region. In the simplest case, the inhomogeneity has the form of "stripes" of charge-rich regions running parallel to the sublattice magnetization, M_s, in neighboring antiferromagnetic regions. The discovery of well defined stripe-like spin density and charge density modulations in La_2NiO_{4+x} [J. M. Tranquada 1994] focused attention on the possibility of an electronic phase separation in the cuprates in general.

ESR experiments were performed on $YBa_2Cu_3O_{6+x}$ single crystals doped with a minute amount of the ESR probe Gd and Ca which introduce a small concentration of electronic holes. Crystals were grown and Raman spectroscopy was performed at the WMI Garching (Germany). Far-infrared spectroscopy in magnetic fields was performed at the National Synchrotron Light source facilities in Brookhaven New York, USA in collaboration with Laszlo Mihaly at Stony Brook University New York. An extensive account has been written

[Jánossy 2007] on the multifrequency ESR, magnetoresistance and magnetic field dependent far infrared investigations in lightly Ca hole doped YBCO single crystals. In this paper we discuss a series of electron spin resonance (ESR) and infrared (IR) transmission experiments in antiferromagnetic (AF), lightly hole doped $YBa_2Cu_3O_6$ in search for the effect of the spatially inhomogeneous ground state on the magnetic and electric properties. ESR satellites of Gd sites with first neighbor Ca atoms showed that holes are not preferentially localized at low temperatures in the vicinity of Ca dopants. We mapped by multi frequency Gd^{3+} ESR the antiferromagnetic domain structure as a function of hole concentration, temperature and magnetic fields up to 8 T. We attributed the hole doping induced rotation of the magnetic easy axis from collateral to diagonal (with respect to the tetragonal CuO_2 lattice) to the pinning of the antiferromagnetic magnetization to a static modulation or a phase separated network of the hole density. The dominantly fourfold symmetry of pinning suggests that the hole density network has also this symmetry and is not a simple array of stripes. There is no magnetic field dependence and no in-plane anisotropy of the infrared transmission polarized in the CuO_2 planes in an x=0.02 crystal placed in magnetic fields up to 12 T. Thus the network of holes is rigid and is not affected by magnetic fields that are, however, strong enough to rotate the AF magnetization into a single domain.

2.2. Fullerene metals, carbon nanotubes and ionic conductors

Fullerene compounds are natural candidates for narrow electronic band systems with strong electronic correlations. Three fullerene systems were investigated in detail: Mg_5C_{60} [Quintavalle 2008], the K doped fullerene-cubane copolymer [Quintavalle 2009] and the Li_4C_{60} fulleride polymer[Ricco 2009]. All three systems are electrically conducting, Mg_5C_{60} and the K doped fullerene-cubane copolymer are metals at high temperatures and insulating at low temperatures due to structural disorder. The magnetic and optical properties of single walled pure and doped carbon nanotubes were studied experimentally and theoretically.

Li_4C_{60} is a most interesting system, as we discovered, it is an ionic conductor. High ionic conductivity in solid state phases is usually observed in strongly disordered or glassy compounds where ions diffuse between a large concentration of unoccupied sites.
The fulleride polymer, Li_4C_{60}, is a different type of ionic conductor as we showed in where we presented a detailed study of the structural, magnetic and transport properties. Ab initio calculations of the molecular structure found intrinsic unoccupied interstitial sites that can be filled by Li^+ cations even in stoichiometric Li_4C_{60} which allows for Li^+ diffusion. The unusually high ionic conductivity (1 S/cm at 650 K) suggests this type of materials may have application in Li ions batteries. For this reason, the work has been widely discussed in the broader scientific community (*see further references in* [Ricco2009]). A publication [Quintavalle2009a] on the high frequency conductivity (dominated by the electronic contribution) and the electron spin resonance results in Li_4C_{60} is under preparation.

2. 3. Organic metals and superconductors

The multifrequency ESR work on organic superconductors and antiferromagnets is an entirely new subject. ESR studies at low frequencies are scarce and controversial in the literature and there is hardly any work at high frequencies. The work accomplished in the project is pioneering. Two BEDT-TTF {bis(ethylenedithio)-tetrathia-fulvalene, or simply: ET} systems have been studied in detail. Single crystals of ET CuMn were synthesized at EPFL

(Switzerland), high quality single crystals of $ET_2Cu(N(CN)_2)X$, X=Cl or Br in our laboratory at BUTE. Further work on other layered conductors is in progress.

2.3.1 Single ion anisotropy in a magnetically dense anisotropic crystal

ESR is a common method to measure the "crystal" or "zero field parameters" that characterize the magnetic anisotropy and the charge distribution surrounding magnetic ions. In dilute systems these parameters are given by the fine structure splitting of the ESR of the magnetic ion. In magnetically dense systems the exchange interaction between ions narrows the fine structure and only a single ESR line appears. The weak crystal fields of e.g. half filled electron shell ions do not affect the low frequency ESR in magnetically dense systems. However, at high magnetic fields and low temperatures the most important crystal field parameters can be determined from the high frequency ESR.

This method has been used to determine the Mn crystal field parameters in the radical cation salt $ET_2MnCu[N(CN)_2]_4$ [Nagy 2009]. The three dimensional polymeric anion network in this salt is unique among the ET_2X materials. The magnetism arises mainly from two-dimensional layers of 5/2 spin Mn^{2+} ions. The 1/2 spin ET cations are weakly coupled to the Mn^{2+} ions and play little role in the low temperature ESR.

A temperature dependent anisotropic ESR shift below 150 K is related to the distortion of the local environment of the Mn^{2+} ions. In the spectrum calculated in the absence of exchange between the ions, the crystal field splits the Mn^{2+} resonance into five allowed transitions between the six S=5/2 Zeeman levels. The relative intensities of the five lines change with temperature as the population of the various Zeeman levels rearranges according to the Boltzmann distribution. At 300 K the spectrum is symmetric around the unshifted -½ –> +½ transition and the intensities of all 5 transitions are of the same order of magnitude. At low temperatures only the -5/2 –> -3/2 transition has a significant intensity.

The exchange interaction between the Mn^{2+} ions narrows the spectrum into a single line at the intensity weighted average of the 5 transitions. Hence the temperature dependence of the relative intensities of the fine structure lines transforms into a temperature dependent shift of the observed exchange narrowed line. A numerical analysis yielded the second order crystal field parameters. The exchange coupling between the Mn^{2+} ions was also estimated from the line width.

2.3.2 Antiferromagnetic mode diagrams in $ET_2Cu(N(CN)_2)Cl$

High frequency magnetic resonance is a most powerful method to determine the interactions in magnetically ordered materials. In a system with more than one sublattice magnetizations each sublattice magnetization is affected by the molecular fields of the other sublattices. As a consequence, the equilibrium magnetization orientations are complicated functions of the external magnetic field. Furthermore, when exciting the system by an oscillating magnetic field, the oscillating sublattice magnetizations produce extra oscillating fields of the same frequency at other sites, resulting in a coupled system with as many resonance modes as the number of sublattices.

Magnetic resonance in the layered organic charge transfer salt, κ-$ET_2Cu[N(CN)_2]Cl$ illustrates the point. It has two structurally different but symmetry-related and chemically equivalent layers in the basic unit. Below the Neel temperature at 27 K, it is magnetically ordered. The four resonant modes found in the high frequency ESR study [Antal2009] confirmed the suggestion of Smith et al. [Smith2004] that it is a four-sublattice canted

antiferromagnet with strong intra-layer interactions and several orders of magnitude smaller inter-layer interactions.

Finding the weak and narrow resonances in an antiferromagnet or a weak ferromagnet is not a simple task. In κ-$ET_2Cu[N(CN)_2]Cl$, isotropic exchange, Dzyaloshinskii-Moriya and anisotropic interactions shift the resonant fields by several teslas in a non-trivial way, and only the high sensitivity of the spectrometer and hints on the most suitable frequencies and magnetic field orientations given by model calculations made the observation of all four magnetic eigenoscillation modes possible. The rotation map of all four modes (Figure 1) has been determined at 111.2 GHz. The data enabled to model with high precision the magnetic interactions between the four sublattices. Most importantly, we find that interlayer magnetic interactions are extremely small.

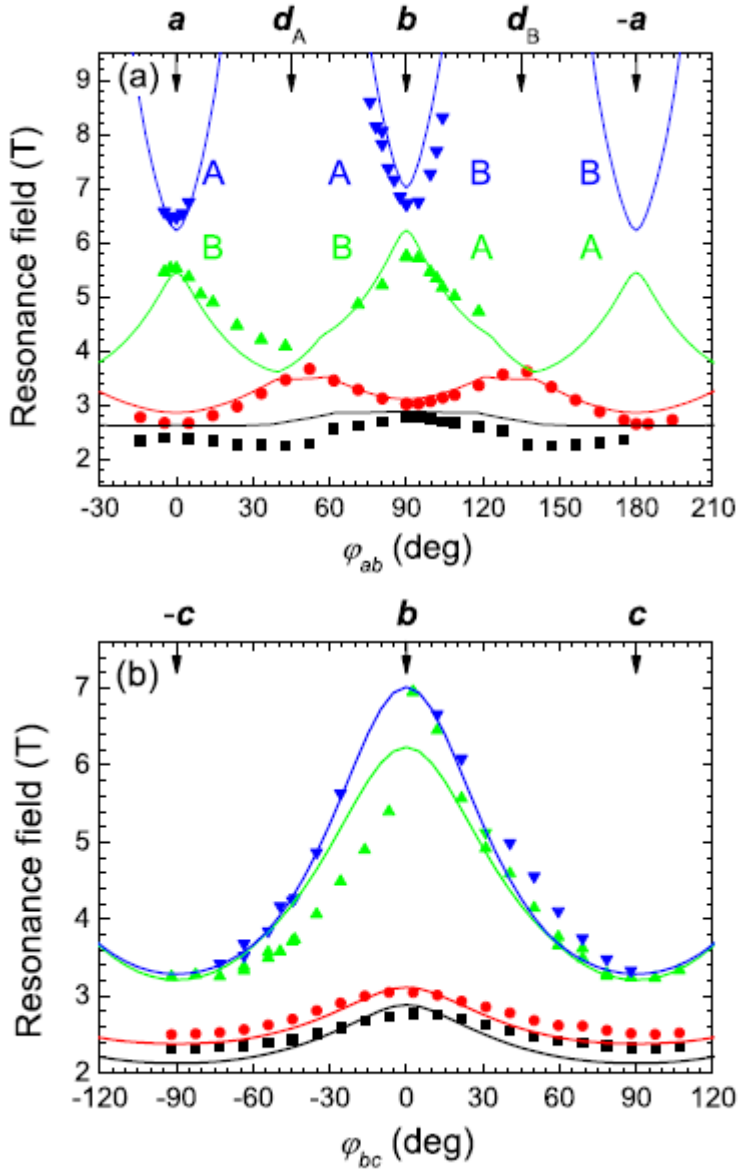

Fig. 1. Observed (symbols) and calculated (lines) AFM resonance magnetic fields of κ-$ET_2Cu[N(CN)_2]Cl$, a four-sublattice canted antiferromagnetic insulator below 27 K, at 111.2 GHz. (a) Sample rotated in the (a, b) plane and (b) in the (b, c) plane. A small interlayer interaction doubles the modes in general magnetic field directions [Antal2009].

2.4. Spin life time in metals, MgB_2

Spin life time in metals is one of the basic quantities to understand their magnetic properties. The standard theory [Elliot 1954], [Yafet 1963] has been established several decades ago. Although experiments were in agreement with theory for many metals, there is a discrepancy in some rather important cases. As our measurement of the spin life time of MgB2 showed [Simon 2007], the Elliot-Yafet theory fails at high temperatures for this material. The temperature dependence of the electron-spin relaxation time in MgB_2 does not follow the resistivity above 150 K; it has a maximum around 400 K and decreases for higher temperatures. This violates the well established Elliot-Yafet theory of spin relaxation in metals. The anomaly occurs when the quasiparticle scattering rate (in energy units) is comparable to the energy difference between the conduction and a neighboring bands. The anomalous behavior is related to the unique band structure of MgB_2 and the large electron-phonon coupling[Simon 2008].

3. Upgrading of the high frequency ESR spectrometer

The research program is based on the multifrequency spectrometer developed at the Budapest University of Technology and a commercial spectrometer at the Chemical Research Centre of the HAS operating in a broad frequency, magnetic field and temperature range. Some ESR experiments at frequencies up to 420 GHz were done at EPFL Lausanne in the laboratory of Professor László Forró.

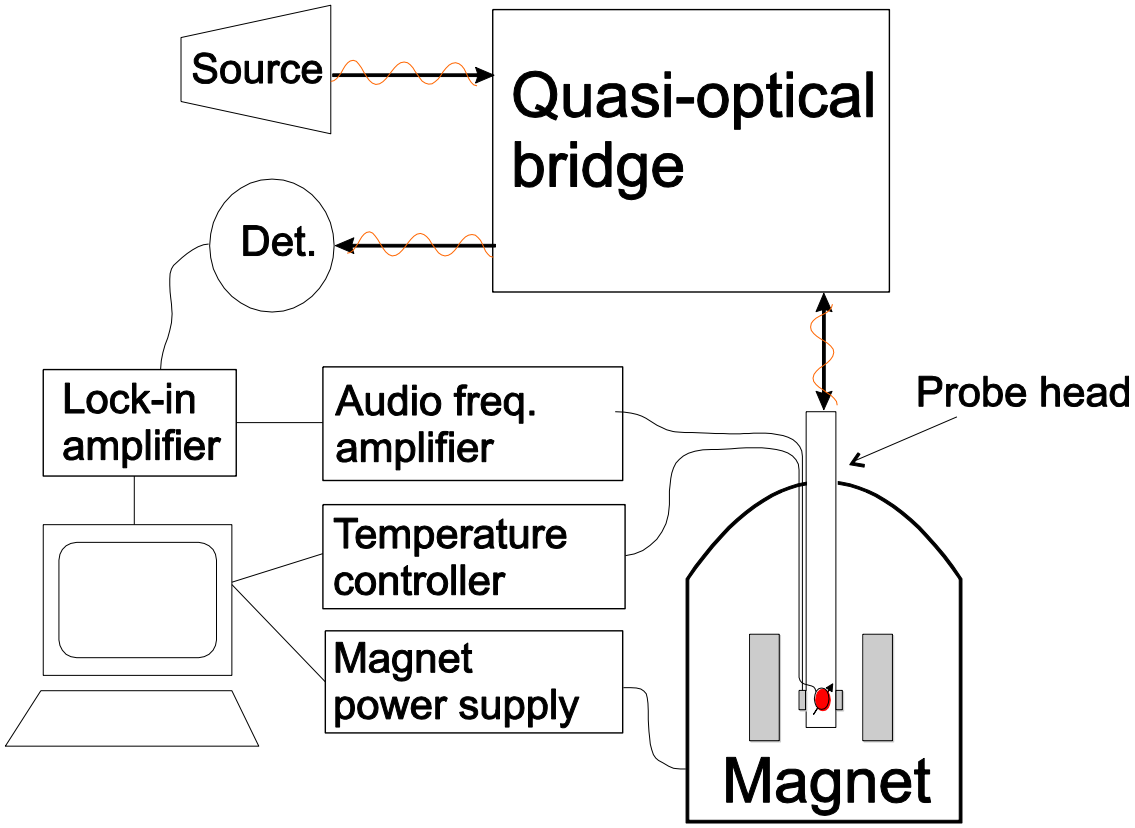

Figure 2. Block diagram of the spectrometer. The quasi-optical bridge transmits the microwaves from the source to the probe head. It filters the signal from the reflected radiation and directs it to the detector. The audio frequency amplifier drives a small coil in the probe head that modulates the magnetic field and the signal of the detector is processed by a lock-in amplifier. The measurement is controlled by a PC.

The high frequency ESR spectrometer was upgraded according to plans. Part of the expenses were covered by a Marie Curie Research Grant obtained by Ferenc Simon. The block diagram of the new spectrometer is shown in Figure 2. The sensitivity at the highest frequency (222.4 GHz) has been increased more than tenfold . The main elements of the high frequency ESR spectrometer reconstruction are shown in Figure 3: a new quasi optical bridge, a powerful mm-wave source, various probe heads and a vibration free supporting structure were installed. The laboratory has been moved to a more spacious room. The quasi optical bridge was designed by Titusz Fehér and András Jánossy. The construction of the spectrometer and

testing were done by Dario Quintavalle and Kálmán Nagy. The high sensitivity of the new spectrometer was vital for the precision studies of the minute high quality single crystals available for cuprates and organic conductors. A description of the modernized high frequency spectrometer and examples for its use in various domains of solid state phyics and biology has been submitted recently for publication. [Nagy 2009b].
A major break down of the superconducting power supply in September 2008 limited available magnetic fields to less than 6 T. The replacement of the power supply is one of the most urgent tasks of the laboratory.

Figure 3. High frequency ESR spectrometer
The sensitivity of the spectrometer was tested on Mn:MgO at ambient temperature. The absolute sensitivity of the spectrometer at 222.4 GHz, calculated for spin 1/2 probes at 300 K is $2 \cdot 10^{10}$ spin/G/$(Hz)^{1/2}$. This is comparable to the sensitivity of modern, commercial X-band spectrometers (Fig. 3.). The corrugated waveguide and Faraday rotators are strongly frequency dependent and the sensitivity is lower at other frequencies; at 111.2 GHz it is about $4 \cdot 10^{11}$ spin/G/$(Hz)^{1/2}$. The mechanical stability of the spectrometer is excellent, the baseline is flat throughout the 0 to 9 tesla sweep.

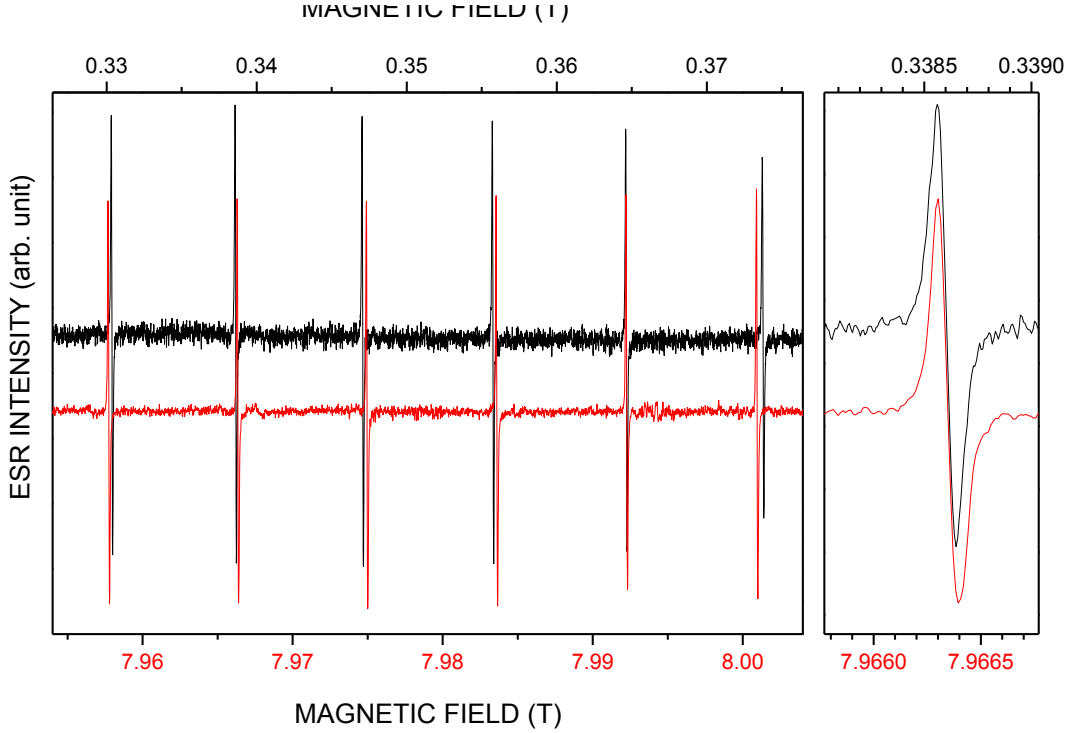

Fig. 4. Comparison of the room temperature spectra of 1mg Mn:MgO powder (Mn concentration 1.58 ppm) recorded in a commercial Bruker Elexsys E500 at 9.4 GHz (upper curve) and in our home-built spectrometer at 222.4 GHz (lower curve). Close-up on the right shows that the line width is 0.1 mT in both measurements thus there is no instrumental broadening. The spectral resolution is 25 times larger at high frequencies.

4. Research team

The research has been conducted by highly experienced seniors, postdoctoral fellows and young students. Electronic maintenance and development was assured by an electronic engineer. High quality organic crystals were grown in a newly set laboratory. A workshop with 2 technicians has been devoted to technical development of the spectrometers, in particular to the construction of the supporting structure and new probe heads.

5. Cooperation with Hungarian and foreign laboratories

The work was based on a cooperation between Hungarian and foreign laboratories:

Budapest University of Technology and Economics, *multifrequency ESR, 3.8 - 225 GHz*
Chemical Research Center HAS, *high sensitivity ESR at 9 GHz*
Research Institute for Solid State Physics and Optics, *fullerene chemistry*
Walther Meissner Institute Garching Germany, *cuprate single crystals, Raman spectroscopy*
Ecole Polytechnique Federale de Lausanne Switzerland *ESR at 420 GHz, organic superconductors*
State University of New York at Stony Brook USA, *far infrared spectroscopy under magnetic field*

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M. Riccò, M. Belli, M. Mazzani, D. Pontiroli, D. Quintavalle, A. Jánossy, and G. Csányi
Phys. Rev. Lett. **102**, 145901 (2009)

The following journals have discussed the implications of this research:

1- Physical Review Focus 23 (story 11), 10 April 2009.
2- Virt. J. Nanosc. Scienc. and Techn. 19 issue 16.
3- La Recherche 431 (June 2009) p.11
4- Pour la Science 380 (June 2009) p.10
5- Materials Research Society Bulletin 34 (July 2009)

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cation salt with quasi-two-dimensional magnetic layers in a
three-dimensional polymeric structure
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Phys. Rev. B in press

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Precise Determination of the Orientation of the Dzialoshinskii-Moriya Vector in κ-(BEDT-$TTF)_2Cu[N(CN)_2]Cl$

Dylan F. Smith, Charles P. Slichter, John A. Schlueter, Aravinda M. Kini, Roxanne G. Daugherty

[Antal2009]
Spin Diffusion and Magnetic Eigenoscillations Confined to Single Molecular Layers in the Organic Conductors κ-(*BEDT-TTF*)$_2$*Cu*[N(*CN*)$_2$]*X* (*X*=*Cl*,*Br*)
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