Giant Negative Magnetoresistance in GdI_2: Prediction and Realization

Giant negative magnetoresistance is a physical property that has recently gained attention when it was realized in multilayer films of metals and then shown to exist in some oxomanganates. It is associated with a significant decrease of the electrical resistance on applying a magnetic field. In the manganates, the effects are sufficiently large that the phenomenon has been termed 'colossal'.

In a systematic search for magnetic analogues (from the electronic structure point of view) of superconductors, our studies have led us to examine GdI_2, a layered d^1 compound which is isostructural with and nominally isoelectronic to the superconductors $2H$-TaS_2 and $2H$-$NbSe_2$. GdI_2 is known to undergo a ferromagnetic transition close to room temperature.

GdI_2 crystallizes with the structure of $2H$-MoS_2, comprising infinite GdI_2 sheets with the Gd atoms in the centers of I_6 trigonal prisms. Each Gd atom is surrounded by six other Gd atoms in the plane at a distance of 407 pm. The structure of GdI_2 is displayed in Fig. 1.

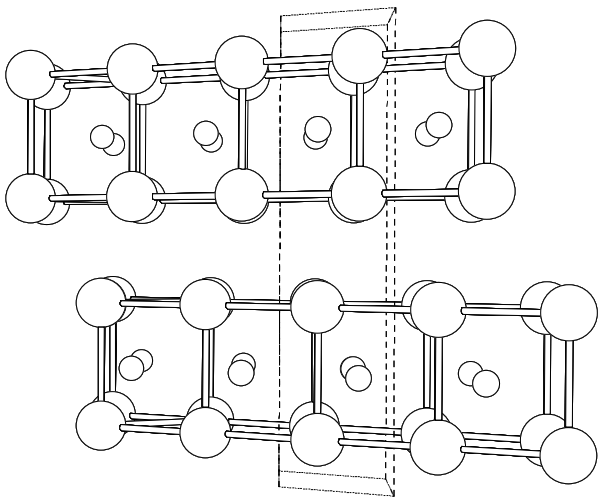

Figure 1: Perspective view of the structure of GdI_2 along [100] of the hexagonal unit cell; large circles cooerspond to I atoms, small circles to Gd atoms, respectively.

Self-consistent, first principles calculations of the electronic structure of GdI_2 were performed using the LMTO method in the Atomic Sphere Approximation (ASA). The scalar relativistic Kohn-Sham-Schrödinger equations were solved taking all relativistic effects into account except for the spin-orbit coupling. k-space integrations used the tetrahedron method to generate 148 irreducible k-points within the Brillouin zone (BZ). The special symmetry points are labelled in accordance with the standard notation of the BZ corresponding to Γ (0,0,0), K ($2/3$,$1/3$,0), M ($1/2$,0,0), A (0,0,$1/2$), L ($1/2$,0,$1/2$) and H ($2/3$,$1/3$,$1/2$) in units of ($2\pi/a$, $2\pi/a$, $2\pi/c$). The band structures are displayed along the lines A-Γ, Γ-M, M-K, K-Γ. The basis set consisted of s, d and f orbitals for Gd and p orbitals for I. The positions and radii of the empty spheres were calculated using an automatic procedure.

The spin polarized densities of states for GdI_2 are separately depicted in Fig. 2 showing the spin-up and spin-down states in the different orbital projections. The spin polarized calculation on GdI_2 yields a magnetic moment of 7.36 $\mu_{\rm B}$ which is markedly enhanced over the value of 7 $\mu_{\rm B}$ expected for the half-filled f band. The system is thus nearly fully spin-polarized. Examining the orbital projected DOS of GdI_2 in Fig. 2, we observe that the f levels are exchange split into spin up and spin down states with a separation of about 4.5 eV. The bulk of the f spin-down states are slightly (0.1 eV) above $E_{\rm F}$. The Gd d bands are split due to the crystal field into lower and upper manifolds in both spin directions. The lower Gd d manifold

crosses $E_{\rm F}$ yielding the result that GdI_2 is a magnetic metal, with the enhancement of the magnetic moment arising from polarization of the conduction band. This results in the Gd spin-up and spin-down d states being separated by about 1 eV. The d states of Gd crossing $E_{\rm F}$ have a bandwidth of a little less than 2 eV. The narrow bandwidth and the implication that electron correlation would be important in GdI_2 has been pointed out previously. The occupied I p bands are stabilized by about 2.5 eV and are centered at around 4 eV below $E_{\rm F}$. The spin polarization leaves the p bands of I completely unaffected.

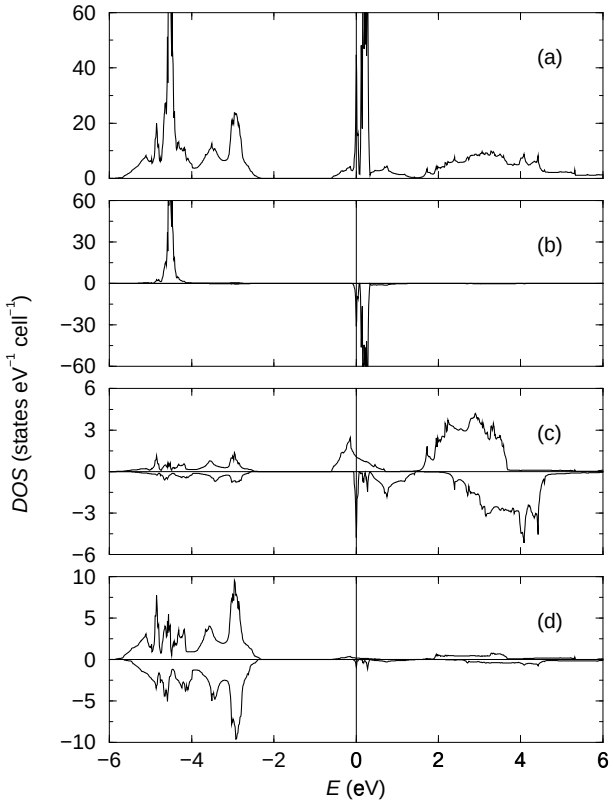

Figure 2: LMTO densities of states for ferromagnetic GdI_2. (a) Total DOS, (b) Spin up and spin down Gd f contributions, (c) spin up and spin down Gd d contributions, and (d) spin up and spin down I p contributions.

The magnetic properties of our samples have initially been characterized by magnetization measurements. Fig. 3 displays the temperature dependence of the magnetization measured in an external field of 10 mT. GdI_2 exhibits spontaneous magnetization below 290(5) K very close to the findings of our preceeding study. At 10 K the saturation magnetization is 7.33(5) $\mu_{\rm B}$, in good agreement with the value predicted by the band structure calculations. The excess of 0.33 $\mu_{\rm B}$ as compared to 7 $\mu_{\rm B}$ expected for seven unpaired electrons of the $4f^7$ configuration of a Gd^{3+} ion has to be attributed to the polarization of the 5d conduction electrons.

The electronic resistance versus temperature measured in various constant magnetic fields up to 7 T (Fig. 3) exhibits a broad anomaly centered at the Curie temperature $T_{\rm c}$. This anomaly shifts to higher temperatures with increasing magnetic field and flattens towards the highest fields. Below 200 K the resistance shows only slight temperature- and field-dependence and increases again towards low temperatures. In view of the pronounced metal-metal bonding in reduced Gd compounds this upturn may indicate the tendency to localization through the formation of local Gd-Gd bonds.

The magnetoresistance -($R(H)$ - $R(0)$)/$R(0)$ (Fig. 3) exceeds values of 60 % at room temperature and high magnetic fields. In small magnetic fields the magnetoresistance, to first approximation, increases with a slope of ≈40%/T at room temperature. At low temperatures we observe a decrease of the magnetoresistance for the highest magnetic fields measured (5 and 7 T), the origin of which is not clear at present.

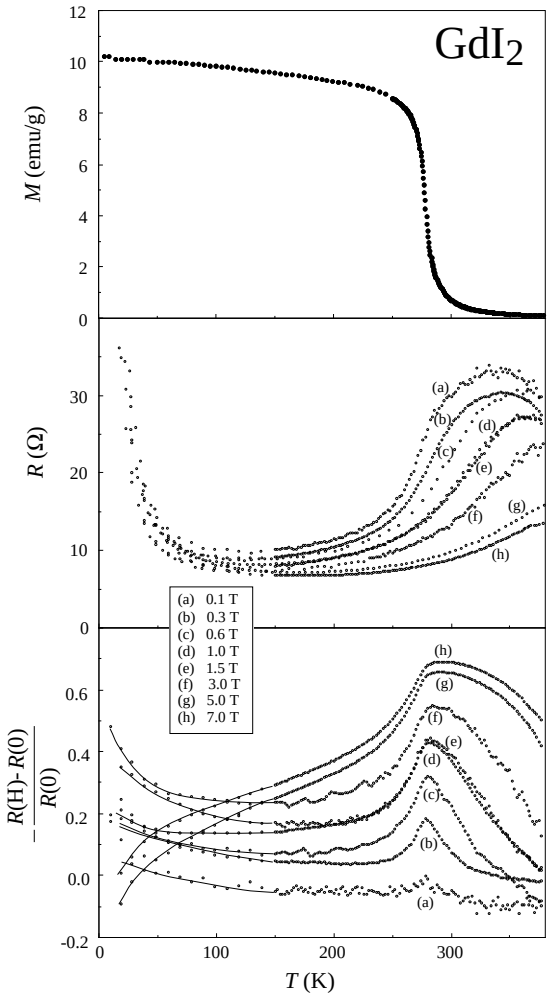

Figure 3: Temperature dependence of the magnetization (B = 10 mT), the resistance of a pellet (diameter 5 mm, 1 mm thickness) and the magnetoresistance –($R(H)$ - R(0))/R(0) of GdI_2.

(K. Ahn, C. Felser (U Mainz), R. K. Kremer, R. Seshadri (U Mainz) and A. Simon)