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Giant negative magnetoresistance in GdI_2

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Abstract

GdI_2 is a layered d^1 compound which is isostructural with and nominally isoelectronic to the superconductors 2H–TaS_2 and 2H–$NbSe_2$. GdI_2 orders ferromagnetically at 276(2) K and displays large negative magnetoresistance ~70% at 7 T close to room temperature. At 10 K the saturation magnetization is 7.33(5) μ_B in good agreement with the value predicted from spin polarized band structure calculations.

Keywords: GdI_2; Giant negative magnetoresistance; Ferromagnetism

1. Introduction

Giant negative magnetoresistance is a phenomenon that has recently gained particular attention when it was realized in multilayer films of metals and then shown to exist in some oxomanganates [1–3]. 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, we examined GdI_2 [4,5], 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 [6,7]. 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 as shown in Fig. 1. Each Gd atom is surrounded by six Gd atoms in the plane at a distance of 407 pm.

In this paper, we report on our study of the magnetoresistance of GdI_2 and use spin polarized band structure calculations to aid in an understanding of the magnetoresistance behavior of GdI_2.

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2. Experiment

GdI_2 was prepared in a solid-state reaction from Gd metal powder and GdI_3. Reactions are run at 1100 K for 3 weeks, finally quenching the sample to room temperature. The reactions were carried out under argon inside welded tantalum tubes that were jacketed in evacuated silica tubes.

Electrical resistance was determined on pressed pellets of 5 mm diameter and a thickness of about 1 mm by the van der Pauw method at temperature 10 K$<T<$380 K and in fields up to 7 T using the cryostat of an MPMS magnetometer (Quantum Design). The pellets were enclosed into a vacuum-tight copper can and pressed onto four gold-plated spring contacts. The magnetic susceptibilities of powder samples (~70 mg) were measured with an MPMS SQUID magnetometer between 10 and 380 K and fields up to 7 T. The sample was contained in dried quartz glass ampoules under 1 bar He exchange gas to provide sufficient thermal contact.

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. The positions and radii of the empty spheres were calculated using an automatic procedure.

3. Result and discussion

The spin polarized densities of states for GdI_2 are

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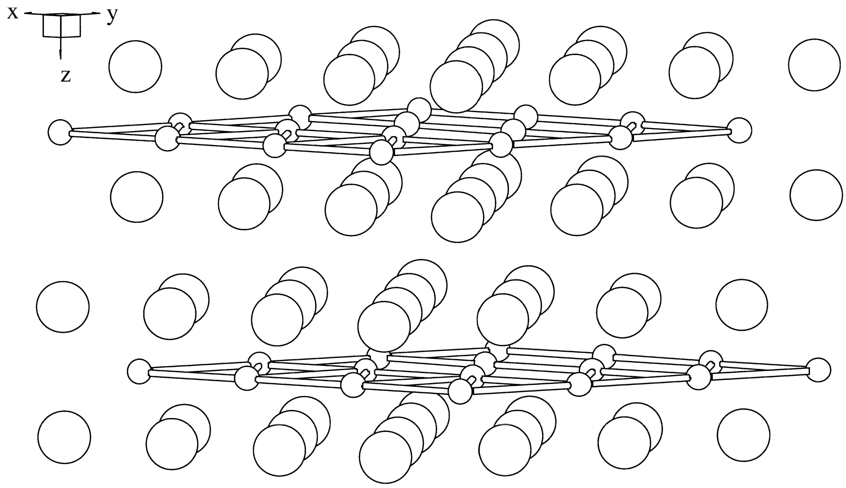

Fig. 1. Perspective view of the structure of GdI_2 along [110] of the hexagonal unit cell; large circles, I atoms.

separately depicted in Fig. 2 showing the spin-up and spin-down states in the different orbital projections. The spin polarized calculation for GdI_2 yields a magnetic moment of 7.36 μ_B which is markedly enhanced over the value of 7 μ_B expected for the half-filled f band. Examining the orbital projected DOS of GdI_2 (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_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_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_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 [8–10]. The occupied I p bands are stabilized by about 2.5 eV and are centered at around 4 eV below E_F. The spin polarization leaves the p bands of I completely unaffected.

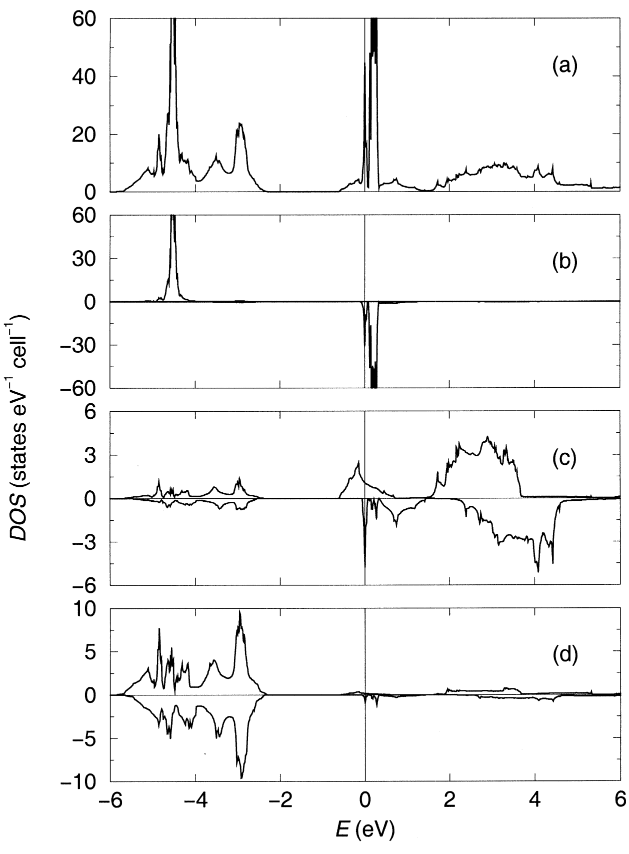

Fig. 2. LMTO densities of states for ferromagnetic GdI_2. (a) Total DOS; (b) spin-up and spin-down Gd f; (c) spin-up and spin-down Gd d; and (d) spin-up and spin-down I p.

The magnetic properties of GdI_2 have initially been characterized by magnetization measurements. Fig. 3a displays the temperature dependence of the magnetization measured for a GdI_2 sample in an external field of 10 mT. GdI_2 was reported to show spontaneous magnetization below 290(5) K [11]. Modified Arrott plots show a Curie temperature of 276(2) K (B.J. Gibson et al., unpublished results), which coincides with the local maxima in the magnetoresistance measurement (Fig. 4b) At 10 K the saturation magnetization of GdI_2 is 7.33(5) μ_B, in good agreement with the value predicted by the band structure calculations. The excess of 0.33 μ_B as compared to 7 μ_B expected for the $4f^7$ configuration of a Gd^{3+} ion is attributed to the polarization of the 5d conduction electrons.

The electrical resistance versus temperature measured (Fig. 3b) exhibits a broad anomaly around 330 K. 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

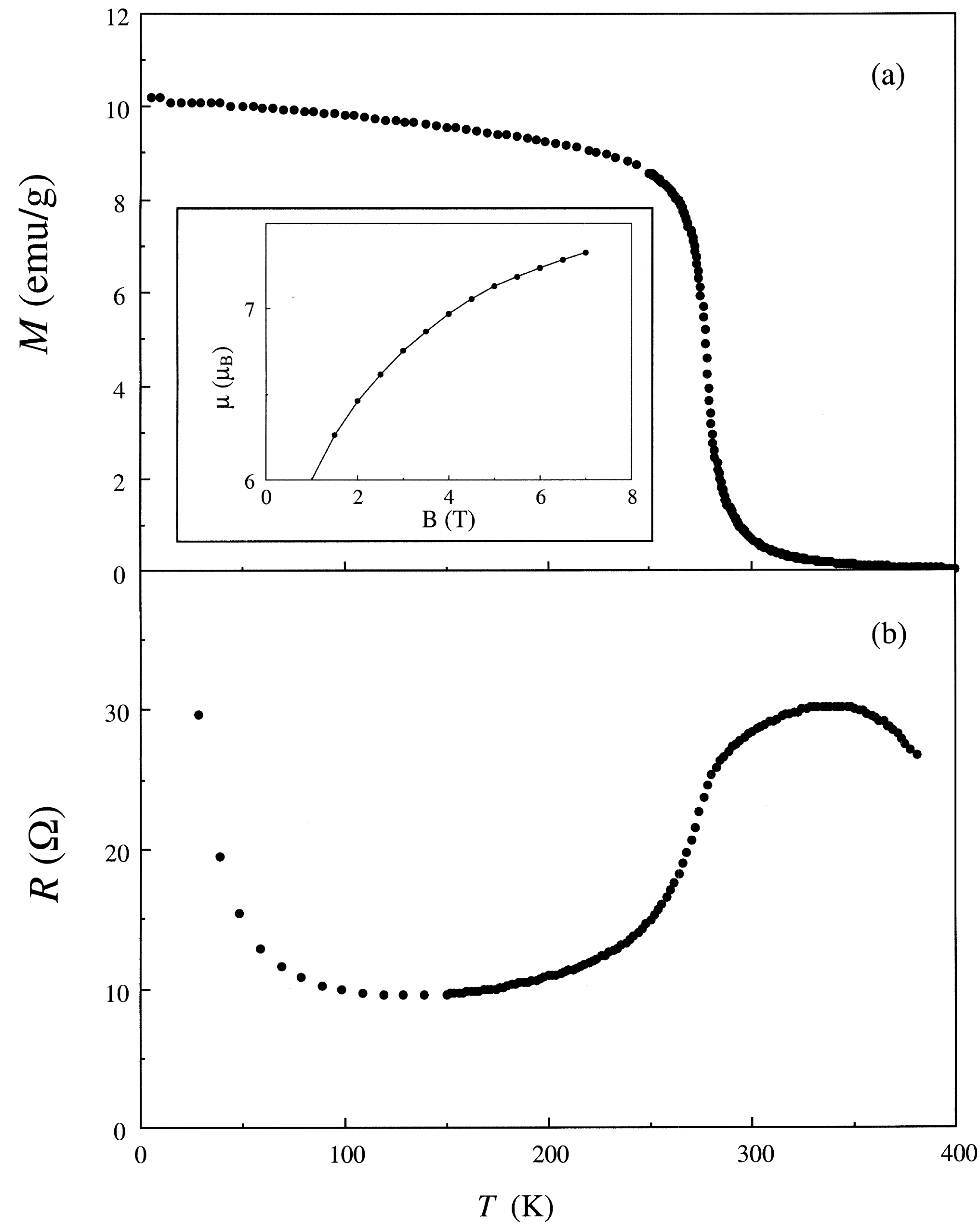

Fig. 3. Temperature dependence of the magnetization of a GdI_2 in a magnetic field of 10 mT. The inset shows magnetization of a powder sample versus magnetic field at 10 K. (b) The plot of resistance versus temperature without field.

and field dependence and increases again towards low temperatures. The physical origin of this behavior is not clear at present and will be discussed in detail in elsewhere [12].

The magnetoresistance $-(R(H)-R(0))/R(0)$ of GdI_2 (Fig. 4) reaches values of about 70% at room temperature and 7 T. In small magnetic fields the magnetoresistance, to a first approximation, increases with a slope of ~40%/T at room temperature (Fig. 5).

4. Summary and conclusion

According to analysis using modified Arrott plots layered GdI_2 shows ferromagnetism below 276(2) K and its saturated magnetization is 7.3 μ_B. Electrical resistance shows an anomaly, such as a broad maximum around 330 K and an increase of the resistance at low temperature. It displays large negative magnetoresistance ~70% at 7 T close to room temperature, which can be understood on the

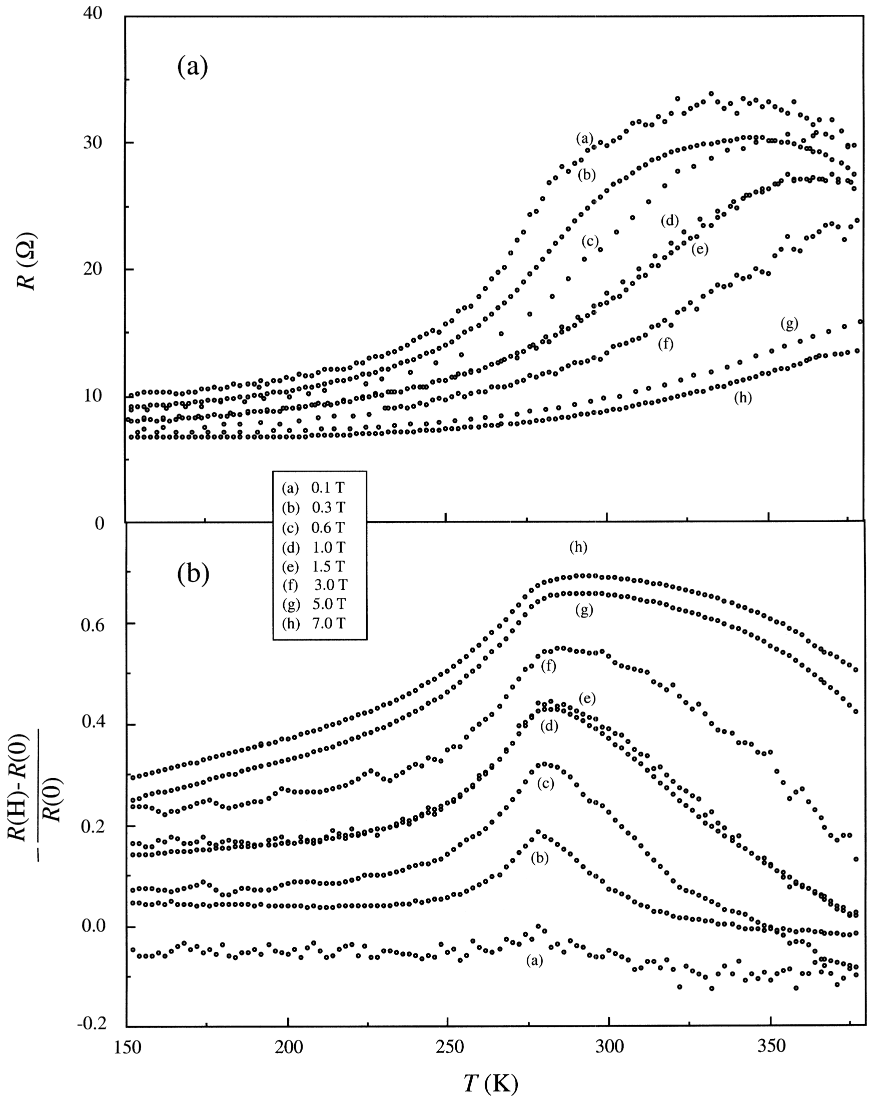

Fig. 4. (a) Resistance of a 5-mm diameter pellet of 1 mm thickness versus temperature. (b) Magnetoresistance $-(R(H)-R(0))/R(0)$ versus temperature for the indicated magnetic fields.

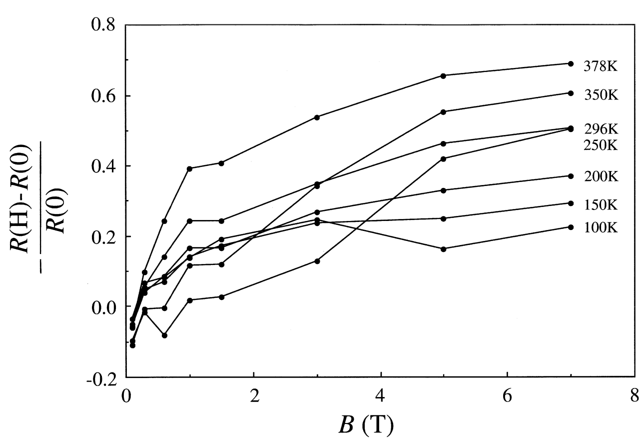

Fig. 5. Magnetic field dependence of the magnetoresistance at constant temperatures as indicated.

basis of band structure calculations. Additional studies of the effect on the magnetoresistance of GdI_2 by doping, e.g., with H, are in progress.

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