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Magnetic Properties and Magnetoresistance of $GdCrSb_3$

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$GdCrSb_3$ is an intermetallic compound with a structure containing alternating layers of Gd and Cr atoms. It undergoes long-range magnetic ordering at 92 K, as revealed by dc and ac magnetic susceptibility measurements, concomitant with a transition in the single-crystal electrical resistivity. These results imply more complicated magnetic behavior than the antiferromagnetism suggested in previous studies. The magnetoresistance measured with the applied field parallel and perpendicular to the *c*-direction (along which are aligned chains of Cr atoms in the structure) shows a strong orientational dependence, consistent with a large magnetic anisotropy expected in this compound.

Introduction

The ternary rare-earth antimonides $RECrSb_3$ were first identified for RE = La, Ce, Pr, Nd, and Sm by Brylak and Jeitschko,[1] and later extended to RE = Gd, Tb, and Dy by us.[2] These compounds have elicited significant interest because of their varied magnetic and electronic transport behavior since we first demonstrated the occurrence of itinerant electron ferromagnetism in $LaCrSb_3$.[3] This is noteworthy because most Cr-containing intermetallic compounds display antiferromagnetism if they undergo magnetic ordering. The unusual properties of the $RECrSb_3$ series ultimately can be traced to the low-dimensional nature of the crystal structure, which consists of anionic ${}^{2}_{\infty}[CrSb_2]^{2-}$ layers and ${}^{2}_{\infty}[Sb]^{1-}$ square nets that are stacked along the *a* direction and separated by RE^{3+} cations (Figure 1). Chains of face-sharing $CrSb_{6/3}$ octahedra extend along the *c* direction; the Cr−Cr distance is half the *c* parameter, or ~3.0 Å. An alternative description draws attention to the close relationship of $RECrSb_3$ to the binary early rare-earth diantimonides $RESb_2$ (RE = La−Nd, and Sm).[4]

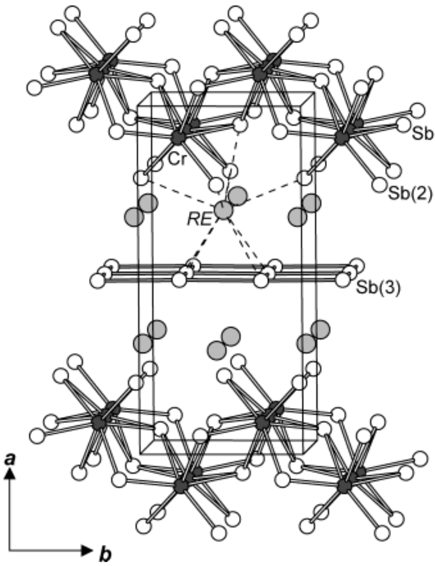

Figure 1. Crystal structure of $RECrSb_3$ (RE = La−Nd, Sm, and Gd−Dy).

The early members of the $RECrSb_3$ series (RE = La−Nd, and Sm) have been studied extensively by magnetic susceptibility,[3−7] electrical resistivity,[6,7] and neutron diffraction[3,4] experiments on powders, and by electrical resistivity,[3,4,8] magnetoresistance,[4,8] and magnetic susceptibility[8] experiments on single crystals. All undergo ferromagnetic ordering below ~125 K. In $LaCrSb_3$, the best investigated member, the magnetic ordering arises solely from the Cr moments. However, the magnetic properties seem to be sensitive to the degree of Cr substoichiometry and the method of preparation. Nevertheless, $LaCrSb_3$ can retain its ferromagnetism despite partial substitution of Cr with other metals.[9] Recent single-crystal neutron diffraction studies suggest that a spin reorientation process occurs within the *bc* plane in the Cr sublattice and imply a revised interpretation in which the metallic magnetism of $LaCrSb_3$ is unconventional, involving the coexistence of local and itinerant moments.[10] In the other $RECrSb_3$ members (RE = Ce, Pr, Nd, and Sm), magnetic ordering of the RE moments, separate from the ordering of the Cr moments, is expected. Only in $NdCrSb_3$ has the detailed

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nature of these ordering processes been unambiguously verified, through neutron diffraction studies.[4] Here, the ferromagnetic Cr moments flip from the *bc* plane to align with ferromagnetic Nd moments parallel to the *a*-axis as the temperature is decreased below 18 K.

The late members of the $RECrSb_3$ series (RE = Gd, Tb, and Dy) have not been examined as thoroughly, probably because they do not display the ferromagnetism observed in the early members. Magnetization studies by Leonard et al. suggest that these compounds are antiferromagnetic, with critical temperatures below 26 K.[6] The independent ferromagnetic ordering of the Cr sublattice now appears to be suppressed, with presumably only coupled RE−Cr magnetic ordering taking place. We report here the magnetic and magnetotransport behavior of $GdCrSb_3$, and show that this compound is not an antiferromagnet with $T_N = 26$ K, as previously reported.[6] Comparison between the single-crystal magnetoresistance (MR) and powder magnetic susceptibility data provides insight into the nature of the magnetism in $GdCrSb_3$.

Experimental Section

Synthesis. Powders of the elements Gd (99.9%, Cerac), Cr (99.95%, Cerac), and Sb (99.995%, Aldrich) were mixed in stoichiometric proportions. The mixtures were pressed into pellets and arc-melted in a Centorr 5TA tri-arc furnace under argon. The samples were reground and heated in fused-silica tubes in vacuo at 800 °C for 8 days. The powder samples used for magnetic measurements were analyzed by powder X-ray diffraction on an Enraf-Nonius FR552 Guinier camera (Cu $K\alpha_1$ radiation; Si standard), which revealed the presence of $GdCrSb_3$ in high purity and the absence of any other rare-earth- or transition-metal-containing binary phases. The composition of crystals used for resistivity measurements was verified by EDX (energy-dispersive X-ray) analysis on a Hitachi S-2700 scanning electron microscope.

Magnetic Measurements. Magnetic data were obtained on a Quantum Design PPMS 9 T magnetometer/susceptometer. Measurements of dc magnetic susceptibility between 2 and 300 K were conducted under zero-field-cooled and field-cooled conditions in an applied field of 1000 Oe. Measurements of ac magnetic susceptibility were made with driving amplitudes between 1 and 5 Oe and with frequencies between 1000 and 5000 Hz. All data were corrected for sample and holder diamagnetism. The results were reproducible and in good agreement with measurements conducted on a separate sample.

Electrical Resistivity. The electrical resistivity of single crystals of $GdCrSb_3$ was measured by standard four-probe ac techniques with a Quantum Design PPMS ac-transport controller (model 7100). The current was 200 μA and the frequency was 16 Hz. The resistivity was measured parallel to the needle axis *c*; crystal dimensions precluded measurements perpendicular to *c*. The crystal was mounted onto a horizontal rotator stage to allow accurate alignment of the needle axis with the applied magnetic field. Isothermal magnetoresistance measurements were taken with two crystal orientations, $H \parallel c$ and $H \perp c$.

Results and Discussion

Temperature Dependence. The resistivity along the needle axis, corresponding to the crystallographic *c*-axis, of a single crystal of $GdCrSb_3$ is shown in Figure 2. Metallic behavior is indicated, with a change in slope in the ρ vs T curve near ~75 K, characteristic of $RECrSb_3$ compounds. The magnitude of the resistivity ($\rho_{300} = {\sim}1 \times 10^{-4}$ Ω cm, $\rho_2 = {\sim}6 \times 10^{-5}$ Ω cm) is similar to that of other $RECrSb_3$ members. The dc magnetic susceptibility (M/H) of a powder sample of $GdCrSb_3$ is shown in Figure 3. The prominent maximum in the curve at 92 K suggests an onset of long-range magnetic ordering. The occurrence of transitions in both the single-crystal resistivity and powder magnetic susceptibility curves at similar temperatures indicates that the magnetic properties of the powder sample are not attributable to an impurity phase. These results appear to contradict previous assertions that $GdCrSb_3$ undergoes antiferromagnetic ordering with $T_N = 26$ K.[6] Although the sample preparation method can lead to differences in ordering temperatures, it should be noted that our sample of $GdCrSb_3$ was also prepared by arc-melting and annealed under conditions similar to those of the previous study. At high temperatures (300 K), the effective moment of $GdCrSb_3$ is 8.16 μ_B/f.u., only marginally larger than that expected for localized Gd^{3+} moments (7.94 μ_B). Because $LaCrSb_3$ contains a nonmagnetic rare-earth component, its room-temperature effective moment (2.60 or 3.68 μ_B/f.u.)[7,8] can be used to estimate the contribution of Cr magnetism in $GdCrSb_3$. With this taken into account, the value of the effective moment observed in $GdCrSb_3$ suggests that there remain significant magnetic interactions between the

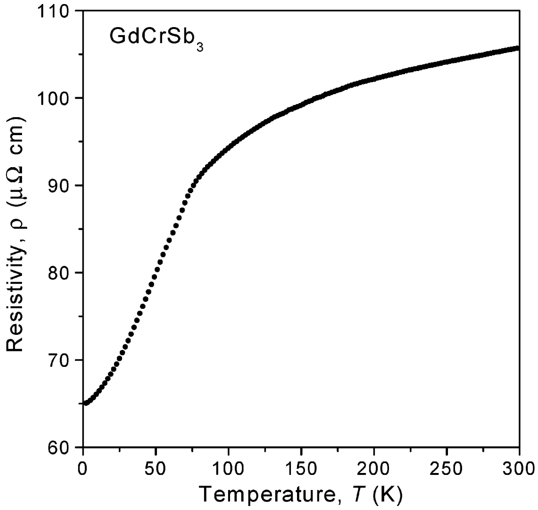

Figure 2. Zero-field electrical resistivity of a single crystal of $GdCrSb_3$ measured along the *c*-axis between 2 and 300 K.

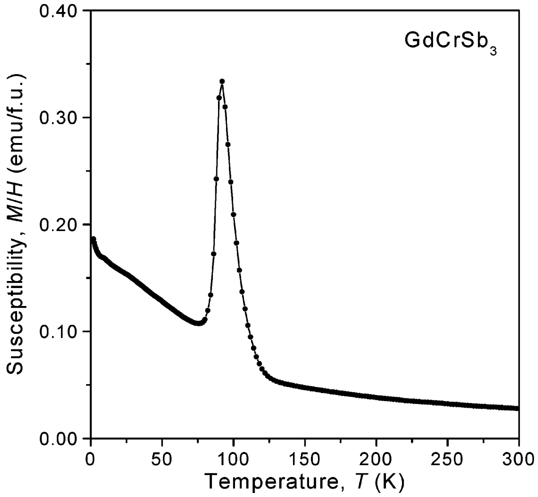

Figure 3. ZFC dc magnetic susceptibility (M/H) of $GdCrSb_3$ powder as a function of temperature ($H_{dc} = 1000$ Oe).

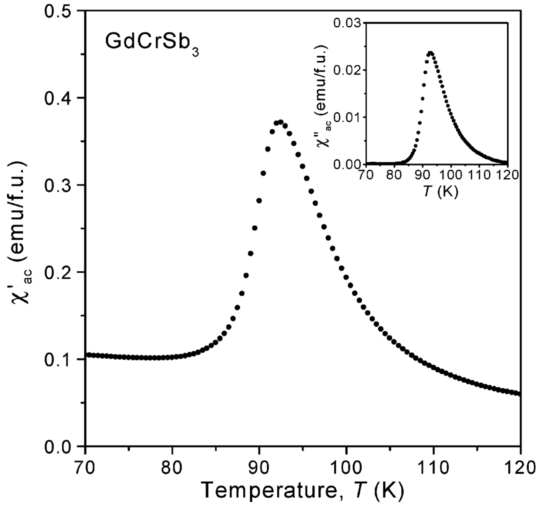

Figure 4. Real and imaginary (inset) components of the ac magnetic susceptibility of GdCrSb$_3$ powder as a function of temperature ($H_{dc} = 0$).

rare-earth and transition-metal moments above the ordering temperature. Strong spin correlations at temperatures significantly higher than T_C have also been reported for LaCrSb$_3$.[10] However, there is evidence for Cr substoichiometry, to as low as 90%, in RECrSb$_3$ compounds;[1,2,4,10] variations in the Cr occupancies may account for differences in the magnetic properties observed in LaCrSb$_3$, such as the saturation magnetization (0.8−1.74 μ_B/f.u.)[3,8] and Cr ordering temperature (125−146 K).[3,5,7]

The electrical and magnetic behavior of GdCrSb$_3$ is characterized by a single transition, in contrast to that for the early members of the RECrSb$_3$ series containing a magnetic RE atom (RE = Ce, Pr, Nd, and Sm), where two transitions are observed, corresponding to the onset of Cr ordering at relatively high temperatures ($T_{Cr} = \sim 120$ K) and coupled RE−Cr ordering at low temperatures ($T_{RE-Cr} = \sim 10$ K), respectively.[4−6] For GdCrSb$_3$ and possibly the other late members of the RECrSb$_3$ series (RE = Tb, Dy), the presence of a single transition could be accounted for by the following possible magnetic structures: (i) the RE atoms are magnetically ordered and the Cr atoms do not possess a magnetic moment, or (ii) the moments of the RE and Cr sublattices are strongly coupled. Either scenario would give rise to a single magnetic ordering temperature, although a conclusive answer can be obtained only from detailed neutron diffraction studies. Unfortunately, naturally occurring Gd consists of isotopes that are high neutron absorbers (^{155}Gd, ^{157}Gd), so neutron diffraction experiments on GdCrSb$_3$ would require isotopically pure samples.

The ac magnetic susceptibility of GdCrSb$_3$ is shown in Figure 4. The observation of an imaginary component (χ''_{ac}) (inset of Figure 4) is consistent with the formation of a magnetically ordered state below 92 K that contains uncompensated spin. Although this could arise from a noncollinear alignment of Gd moments, it is likely that some type of ferrimagnetic structure is formed between the Gd and Cr moments. The orientation of the uncompensated spin cannot be determined from these powder data; measurement of the magnetic susceptibility of a large single crystal is required. The magnetization about the ordering temperature was acquired under zero-field-cooled (ZFC) and field-cooled (FC) conditions with $H =$ 10, 100, and 500 Oe (not shown). No bifurcation in the magnetization signal was observed under these conditions.

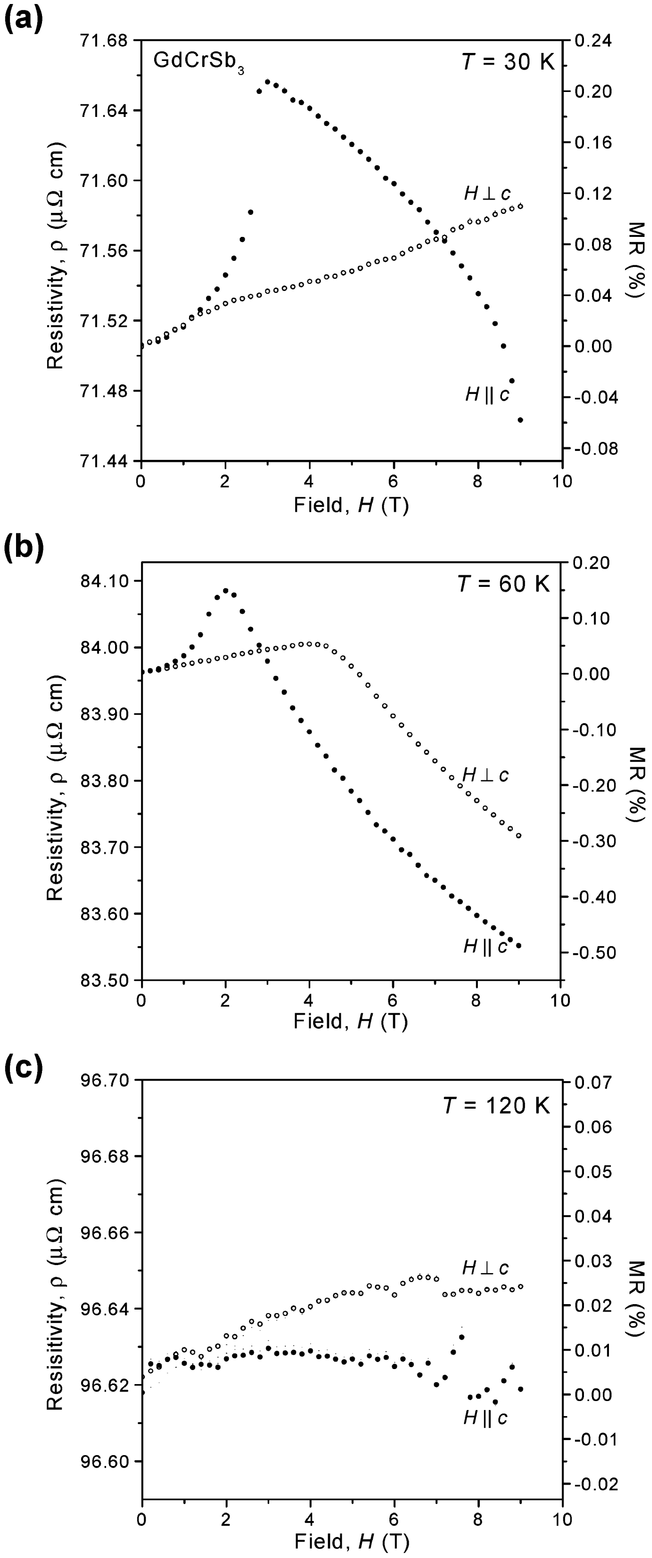

Figure 5. Magnetoresistance of a single crystal of GdCrSb$_3$ measured along the *c*-axis with the fields applied parallel and perpendicular to this axis at (a) 30 K, (b) 60 K, and (c) 120 K.

Field Dependence. The magnetoresistance (MR(%) $= [(\rho(H) - \rho(0))/\rho(0)] \times 100$) of GdCrSb$_3$ is shown in Figure 5. The MR is strongly field dependent below the

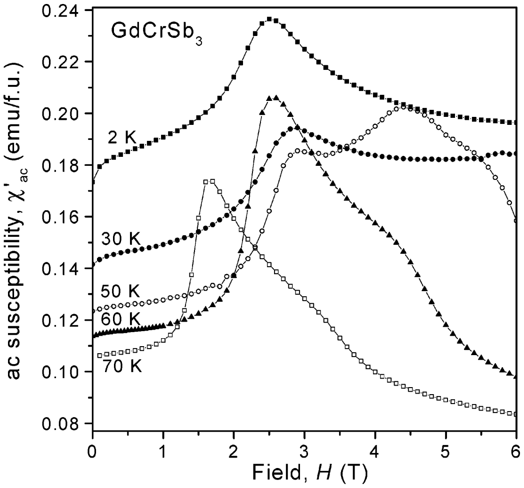

Figure 6. Real component of the ac magnetic susceptibility of GdCrSb$_3$ powder as a function of field at various temperatures.

ordering temperature (30 and 60 K), but only very weakly dependent above it (120 K). Below 92 K, the MR is positive and increases up to a critical field H_C. This observation is consistent with an antiferromagnetic ordering of moments, followed by a metamagnetic transition at H_C.[11] When the temperature is decreased under ZFC conditions to 30 K, the MR is +0.2% at the critical field $H_C = 3$ T when $H \parallel c$ (Figure 5a). In this orientation, the needle axis of the crystal is aligned with the applied field, placing the chains of Cr atoms in the crystal structure parallel to the field. At 30 K, there is no maximum in the MR curve when $H \perp c$. This result is consistent with the antiferromagnetic spins being aligned along the c axis. As the applied field is increased, spin fluctuations in the sublattice aligned antiparallel to the field are enhanced, increasing the MR. When the applied field reaches H_C, the antiparallel spins realign with the field. Any further increase in applied field causes a reduction in spin fluctuation, decreasing the MR.

At 60 K, critical fields are observed at 2 T when $H \parallel c$ and at 4.2 T when $H \perp c$, with a less dramatic field dependence in the MR for the latter orientation (Figure 5b). The MR is negative above the critical fields, but very large applied fields are required to induce a value of −0.5%. There may exist another magnetically ordered phase not observed at 30 K, with the field-induced transition causing the spins to reorient onto the *ab*-plane. Because the same crystal mount was used for all MR measurements, errors arising from variations in crystal position can be ruled out as the source of the different MR behavior at 30 and 60 K.

The transitions in the single-crystal MR curves correlate well with transitions seen in field-dependent ac susceptibility measurements on the powder sample of GdCrSb$_3$ (Figure 6). At 30 K, there is a transition at $H_C = 3$ T, in good agreement with the MR data. As the temperature is increased, a second field-induced transition emerges. At 60 K, the two maxima in the ac susceptibility curve occur at $H_{C1} = 2.6$ T and $H_{C2} = 4.3$ T, very close to the two critical fields observed in the MR data.

These field-dependent MR and ac susceptibility data suggest the existence of two magnetically ordered phases between 50 and 92 K. The absence of the second field-induced transition in the 2 and 30 K curves in Figure 6 limits the occurrence of the high-field phase to only the higher temperature portion of the magnetic phase diagram. The zero-field ac susceptibility data indicate an ordered phase below 92 K, placing the low-field phase with a net moment possibly arising from a canted antiferromagnetic alignment of localized Gd^{3+} and itinerant Cr moments.

In conclusion, the magnetic behavior of GdCrSb$_3$ is more complicated than previously believed, given the evidence for one temperature-induced and two field-induced transitions that are related to the pronounced anisotropy of the RECrSb$_3$ structure. More detailed studies of the magnetic and electronic structure of GdCrSb$_3$ seem worthwhile, as would reexamination of the other late members of the RECrSb$_3$ series (RE = Tb, Dy).

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