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Field-induced magnetic phase transitions in a GdSi single crystal

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We report on unusual field-induced magnetic phase transitions observed in a GdSi single crystal at low temperature. The magnetization curves initially show an anisotropic character between the *b* axis and the *ac* plane. With increasing applied field, the magnetization measured along the *c* axis merges with that measured along the *b* axis through a jumplike transition at field of about 2.5 T, whereas that measured along the *a* axis gradually joins the other two at about 3.8 T. Above 3.8 T, the magnetization behaves isotropically with applied magnetic field and then reaches saturation through a jumplike transition at a field of about 19.5 T. We discuss the anomalous behavior of the compound in terms of interplay between the localized $4f$ spins and the (itinerant) conduction electrons.

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The dominant source of magnetic anisotropy (MA) in rare-earth-based materials is a single-ion anisotropy, which arises from the interaction between the crystalline electric field and the electric multipole moments of the $4f$ charge cloud.[1] In the rare-earth metals, the typical anisotropy energy is of the order of meV/atom. An exception, however, is Gd where the angular momentum L is zero and the moments have a pure S-state character implying absence of the electric multipole moments.

The origin of a small MA of 35.4 μeV/atom[2] found in Gd metal has been the subject of extensive discussions. One possible source is the dipole-dipole interaction,[1,3–6] which can account for 7.5 μeV/atom. Recently, from first-principles calculations, Colarieti-Tosti *et al.*[7] indicated that the remaining part of the MA in Gd metal should come from the conduction electrons (the itinerant $5s$, $5p$, $6s$, $6p$, and $5d$ ones). In this case, the localized $4f$ spins polarize the conduction electrons via exchange interaction, which, in turn, transfers the MA of the conduction electrons to the $4f$ spins. The calculated MA appears to depend on very fine details of the band structure. In fact, these calculations are consistent with the observation of Franse and Gersdorf[2] that Fermi surface effects are to be taken into account.

In Gd compounds, the presence of a MA so far has largely been attributed to dipole-dipole interactions.[8,9] In few cases, the crystal field and exchange effects coming from higher multiplets have been discussed as possible sources.[10,11] Again, the MA in Gd compounds is usually of the order of less than a few tens of μeV/atom.[9]

In this connection, the results reported recently for a polycrystalline GdSi sample are surprising. This compound crystallises in the FeB type of structure with space group *Pnma*.[12] In this structure, the orthorhombic unit cell contains four formula units with all the atoms occupying the Wyckoff position (4c) of the *Pnma* space group. GdSi orders antiferromagnetically below T_N of about 55 K.[13,14] The high-field measurements of the magnetic isotherm at 4.2 K on a (polycrystalline) bulk sample revealed that the slope of the magnetization curve changes at an applied field B of about 3 T, and is then followed by a jumplike phase transition at 19.7 T.[13] In the high-field free-powder (HFFP) measurements, this high-field transition was also observed at about the same field strength.[14] A fitting, using the theoretical model developed for the HFFP method,[15] gives a value of the anisotropy constant K_1 of about 376 μeV/atom. This value, however, is about one order of magnitude larger than the MA of any of the Gd compounds known so far. In order to understand the anomalous features of GdSi, in the present paper, we report on detailed investigations, performed on a single-crystal sample.

A GdSi single crystal was grown in a mirror furnace using the floating zone technique. The seed and feed for crystal growth were prepared by arc melting Gd and Si (with purity of at least 99.9%) to obtain an alloy button of the nominal composition GdSi. In the most stable growth, we used a growth rate of 6 mm/h, and a rotation of the seed and feed of 30 rpm in opposite directions.

The measurements of the temperature dependence of the magnetization were carried out in a commercial Quantum Design SQUID magnetometer in the temperature range 2–300 K. For the determination of the field dependence of the magnetization, we used both a 12 T Oxford Vibrating Sample Magnetometer (VSM) and the 40 T pulsed field installation at the University of Amsterdam. The heat capacity measurements were performed in the temperature range 0.45–300 K using a Quantum Design Physical Property Measurement System (PPMS) with a heat capacity option.

In Fig. 1, we present the zero-field-cooled (ZFC) magnetization, measured in a field of 0.1 T, as a function of temperature. The antiferromagnetic ordering of the compound takes place below $T_N = 55$ K. Below the ordering temperature T_N, we also observe another peak at around 3.5 K. A remark-

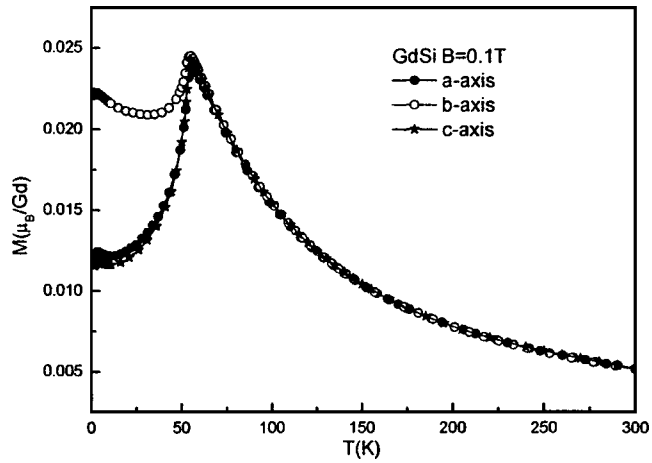

FIG. 1. Temperature dependence of the magnetization of the GdSi single crystal, measured in an applied magnetic field of 0.1 T along the main axes.

able feature of the compound is the anisotropy observed below T_N. We already mentioned earlier that such an anisotropic feature is usually not expected for the *S*-character moment of the Gd compound. We can see from Fig. 1 that the susceptibility measured along the *b* axis is higher than that measured along the *a* and *c* axes. Above T_N all the ZFC curves coincide. Fitting with a Curie-Weiss behavior $\chi = C/(T-\theta_p)$ yields an effective moment $\mu_{\text{eff}}=8.4\mu_B$ and the Weiss temperature $\theta_p=-1.63$ K. The value of μ_{eff} is higher than that of 7.9 μ_B expected for a free Gd^{3+} ion. This clearly indicates that there is a contribution of the conduction electrons to the overall measured moment of the compound.

To investigate the properties of the compound into more detail, we have measured the magnetic isotherms at 4.2 K in fields up to 40 T. The results, as displayed in Fig. 2, are quite remarkable. We observed that (i) along the *b* axis the magnetization increases (almost) linearly with increasing magnetic field until 19.5 T. (ii) Along the *c* axis, the magnetization curve initially coincides with that measured along the *a* axis. At $B_1 \sim 2.5$ T, a jumplike phase transition occurs beyond which the magnetic isotherm merges with that measured along the *b* axis. (iii) Along the *a* axis, the transition is of second order starting from $B_1 \sim 2.5$ T to $B_2 \sim 3.8$ T. (iv) Above B_2, the compound behaves isotropically, and eventually another jumplike transition occurs at $B_3 \sim 19.5$ T leading to saturation. The value of the saturation magnetization is 7.3 μ_B/Gd, higher than 7 μ_B/Gd expected for a free Gd^{3+} ion.

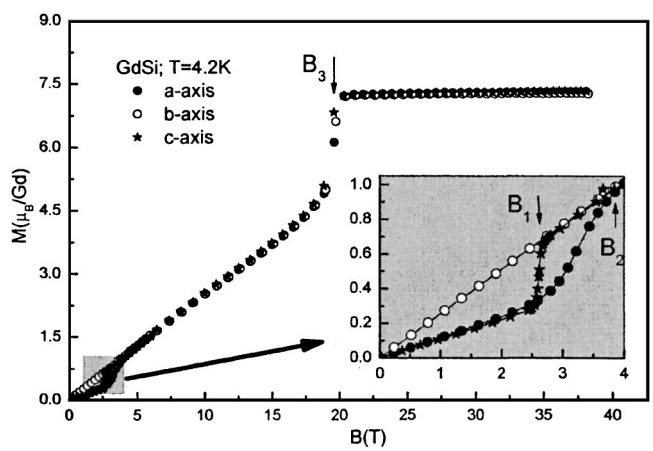

FIG. 2. Field dependence of the magnetization of the GdSi single crystal measured at 4.2 K. The inset shows an extended view at low fields.

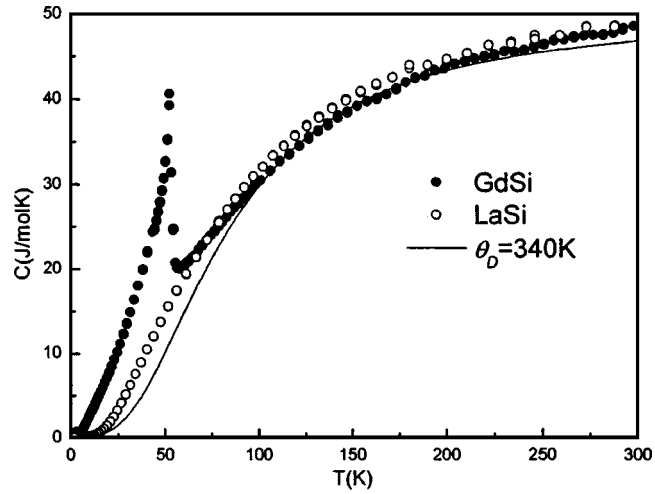

FIG. 3. Heat capacity versus temperature for the GdSi and LaSi compounds. The solid line presents the Debye function fitting with a Debye temperature $\theta_D=340$ K.

We have also performed heat capacity measurements. The results measured in zero field are presented in Fig. 3. At 55 K, a λ-like peak is observed, which, in this compound, is a characteristic for the transition from paramagnetic to antiferromagnetic order. There is also another tiny peak at 3.5 K, consistent with the ZFC data. This low-temperature peak is probably related to the presence of a small amount of impurity phase in the crystal, too small (say <5%) to be detectable in our x-ray data (data not shown), although it cannot be ruled out that it is caused by some intrinsic band structure effect.

In Fig. 3, we also include the data of the heat capacity measured on a polycrystalline sample of the isostructural nonmagnetic compound LaSi. The heat capacity of LaSi becomes larger than that of GdSi at temperatures above 80 K. Therefore, LaSi is not a good starting point to obtain the phonon contribution of GdSi by Debye temperature renormalization[16] YSi and LuSi have a different crystallographic structure from that of GdSi, and thus they cannot be used for estimating the phonon contribution in this case. In order to avoid unphysical negative values of the magnetic contribution to the specific heat (C_{mag}) obtained by subtraction of the LaSi data, we also use a calculated Debye function $f_D(\theta_D)$ (Ref. 17) to fit the high-temperature part (i.e., above 55 K) of GdSi. The best fit is given in Fig. 3 with a Debye temperature of $\theta_D=340$ K.

In Fig. 4, we plot the magnetic contribution to the specific heat C_{mag} obtained by subtracting, from the GdSi data, either the data of LaSi or the calculated $f_D(\theta_D=340\text{ K})$ values. The corresponding temperature dependencies of the magnetic entropy are displayed in the inset of Fig. 4. Evidently, the sub-

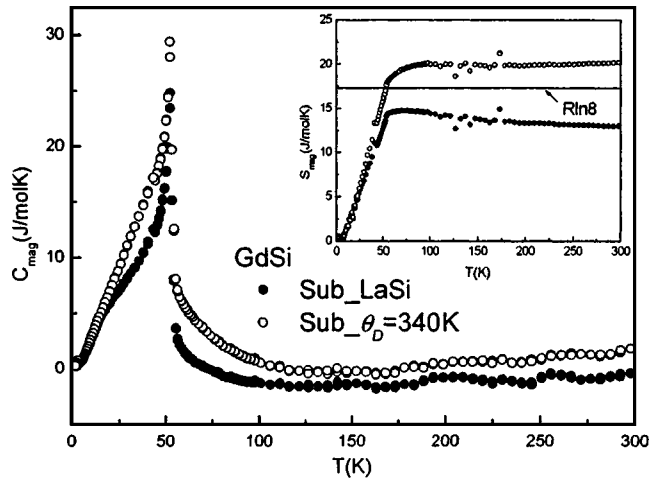

FIG. 4. Temperature dependence of the magnetic contribution to the specific heat C_{mag}. The inset shows the temperature dependence of the magnetic entropy S_{mag}.

traction of the phonon contribution calculated by using $f_D(\theta_D=340\ \mathrm{K})$ does avoid negative values of C_{mag}, but it leads to too large values of the magnetic entropy at high temperatures. The value obtained is of about 20 J/mol K to be compared with a maximum value of 17.3 J/mol K expected when the ground state level is assumed to be $(2J+1)$-fold degenerate in the paramagnetic regime for free Gd^{3+} ions. On the other hand, the subtraction by the LaSi data gives negative values of C_{mag} at high temperature. The maximum magnetic entropy S_{mag} obtained by this subtraction procedure is only 15 J/mol K.

Although the two aforementioned subtraction procedures appear not to be appropriate for GdSi, they should still give a good estimation of the magnetic contribution to the heat capacity of the compound. At the ordering temperature $T_N=55$ K, we obtain $C_{mag}=24.8$ J/mol K and 29.4 J/mol K corresponding with the subtraction of the LaSi data and the $f_D(\theta_D=340\ \mathrm{K})$ values, respectively. Theoretical calculations for Gd compounds[8,18] have indicated that C_{mag} reaches a maximum value of 20.15 J/mol K for the equal moment cases. In the amplitude modulated magnetic structures, the value of C_{mag} is largely reduced and the λ-like shape is smoothed off at T_N. The high value of C_{mag} as well as the well-defined λ-like peak shape obtained at T_N for the heat capacity of GdSi would indicate that the compound has a simple magnetic structure with equal moments.

The phase transitions observed in the magnetic isotherms at low and high applied magnetic fields are far more of puzzling. Since the MA is lost at applied fields $B>3.8$ T, any "*conventional*" source, e.g., dipole interaction, can be ruled out. We also note that our observed field-induced transitions in GdSi are (essentially) different from those in some Gd compounds (e.g., $GdRu_2Si_2$ and $GdRu_2Ge_2$) in which there exists an anisotropic exchange interaction.[19] In the latter case, the MA is not lost by an applied magnetic field and there is also a difference of the saturation fields along the different crystallographic axes. We argue that such a field dependent character of the MA in the GdSi compound can be understood in terms of a contribution from the conduction electrons. The $4f$ spin polarizes the conduction electrons via exchange interactions which transfer the MA of the conduction electrons to the $4f$ spins. In low applied fields, the higher magnetization observed along the b axis would indicate that the moments are more or less confined to the ac plane. On the other hand, when applying a magnetic field, the (slightly) bending of the $4f$ spins leads to a change in the polarization of the conduction electron band, and results in a change of the corresponding MA. At fields above 3.8 T, it appears that the conduction electrons no longer contribute to the MA and the magnetization curve becomes isotropic along all directions. Our argument here is, somehow, consistent with the band structure calculation in some ferromagnetic Gd-Fe and Gd-Co compounds[20] which revealed a strong reduction of the on-site conduction electron spin density of the Gd atoms when the Gd moments are forced into a direction antiparallel with the local exchange field, i.e., parallel with the $3d$ moments. In this connection, it is interesting that in GdSi, a field-induced change in the conduction electron spin density seems to be already significant in low fields, but apparently is (virtually) unchanged in intermediate fields between $B_2=3.8\ \mathrm{T}<B<19.5\ \mathrm{T}=B_3$. At B_3, an identical jumplike phase transition is observed along all the main axes. This transition is clearly not MA related as previously assumed in the HFFP results[14] but it would suggest another significant change in the conduction electron spin density. From the value of the saturation magnetization, we can derive that, after the transition, the conduction electron band contribution is about 0.3 μ_B/Gd and it is parallel to the $4f$ contribution. The magnitude of the jump at B_3, however, is about 2 μ_B/Gd, which is much higher. It seems to us that, in this case, there is a two-way effect in that the field-induced change of the conduction electron spin density also leads to at least a weakening of the interaction between the $4f$ spins. As a result, at B_3, there is also a further sudden change in the spin configuration from the bending towards a (forced) parallel state.

In summary, we have studied the magnetic properties of a GdSi single crystal. The compound reveals extraordinary magnetic phase transitions in the magnetization curves. We propose that the observed MA as well as the jumplike phase transition of the compound at low and high applied magnetic fields, respectively, are due to some fine details of the band structure of the itinerant (conduction) electrons that are coupled to the localized $4f$ spins. The results on GdSi clearly indicate an important influence of the conduction electrons in mediating the $4f$ interactions and determining the magnetic properties of the compound. High-field measurements in static fields to get some information on possible hysteresis effects as well as the magnetic structure determinations using hot neutrons are currently being in progress. To check the validity of our proposed mechanism, a band structure calculation for the GdSi compound would be most helpful.

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