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Magnetic properties of tetragonal $DyRu_2Si_2$

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Abstract. A detailed study of the magnetic properties of the tetragonal rare earth compound $DyRu_2Si_2$ is presented. Magnetization measurements on a single crystal as well as specific heat and resistivity measurements on a polycrystal show features which are typical of a long-period commensurate system in the presence of a huge uniaxial anisotropy. Multistep metamagnetism occurs below the Néel temperature $T_N = 29$ K, in particular at low temperatures. In the low-field low-temperature region, a new magnetic phase has been discovered with an anomalous behaviour.

1. Introduction

For the last few years, many detailed qualitative as well as quantitative magnetic studies have been devoted to ternary rare-earth compounds of the type $RM_2M'_2$ (R $\equiv$ rare earth; M $\equiv$ 3d, 4d or 5d metal; M′ $\equiv$ Si or Ge) [1]. Most of these intermetallic compounds crystallize in the body-centred tetragonal structure of $ThCr_2Si_2$ type (space group, $I4/mmm$). Of the numerous series, the RRu_2Si_2 series is worth studying because of the great diversity of its magnetic properties. In particular, $CeRu_2Si_2$ has been widely investigated, owing to its heavy-fermion properties [2]. Most of the other compounds within the series have been previously studied in polycrystalline form [1]; they exhibit interesting magnetic properties owing to long-range oscillating exchange interactions mediated by conduction electrons. It was shown that RRu_2Si_2 compounds (R $\equiv$ Y, La or Lu) are Pauli paramagnets while RRu_2Si_2 (R $\equiv$ Dy, Tb, Ho or Er) were reported to be antiferromagnetic. $PrRu_2Si_2$ is a ferromagnet [3] while $NdRu_2Si_2$ [4] exhibits two successive magnetic transitions at 10 K and $T_N = 26$ K; below T_N, it develops a sine-wave modulation and below 10 K a ferromagnetic order takes place. Among the heavy rare-earth compounds of this series, $GdRu_2Si_2$ [5] and $TbRu_2Si_2$ [6] show anisotropic multistep metamagnetism.

Recently, a detailed study of $DyRu_2Si_2$ has been carried out by means of powder neutron diffraction as well as magnetization and Mössbauer measurements on a polycrystal [7]. The main relevant conclusions are the following.

(i) In the whole ordering range below $T_N = 29$ K, the structure is described by the same propagation vector $Q = (\frac{2}{9}, 0, 0)$.

(ii) As the temperature is lowered, the squaring up of the modulation becomes visible at 19 K and is complete (antiphase structure) below about 5 K. The amplitudes of the M_Q and M_{3Q} harmonics vary continuously with the temperature.

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(iii) The crystal-field ground state is almost a pure $|\pm\frac{15}{2}\rangle$ state in the paramagnetic phase. The first excited $|\pm\frac{13}{2}\rangle$ doublet is expected to be around 100 K above.

(iv) A rapid increase in susceptibility is observed at very low temperatures for a magnetic field of 1 kOe. This 'divergence' has been attributed to the ferrimagnetic-like behaviour of $DyRu_2Si_2$ at low temperatures owing to the non-compensation of its antiphase structure (five moments *up* and four moments *down*).

(v) As expected in systems with a strong uniaxial anisotropy favouring the c axis, a multistep metamagnetic behaviour is observed at low temperatures, although the measurements were made on a polycrystal.

In the present work, susceptibility and magnetization measurements performed on a single crystal, grown by the tri-arc Czochralski method, are presented, for a magnetic field applied along and perpendicular to the *c* axis (sections 2 and 3). From these results, a new phase has been discovered in the low-field low-temperature range (below $T_t = 3.6$ K at $H = 0$ kOe), with an anomalous behaviour, as shown by the specific heat and resistivity measurements on a polycrystal (sections 4 and 5). Finally, section 6 is devoted to a discussion of all experimental results and to a comparison of those results with previous studies to try to understand the surprising behaviour at low temperatures.

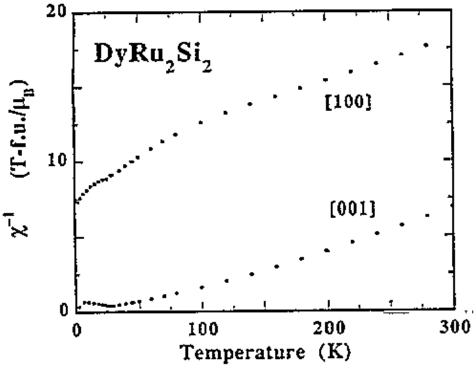

Figure 1. Temperature dependence of the reciprocal paramagnetic susceptibility of $DyRu_2Si_2$ parallel and perpendicular to the [001] axis.

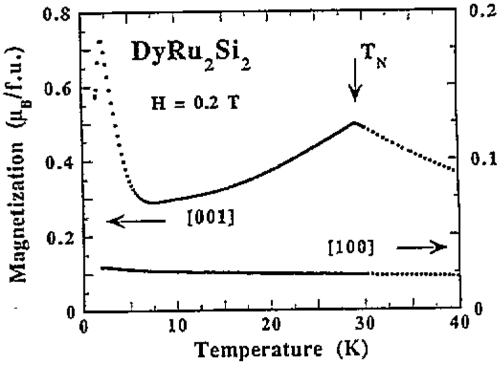

Figure 2. Low-temperature variation in the magnetization along the [001] and [100] axes in a constant magnetic field strength of 0.2 T for $DyRu_2Si_2$. Note the different scale for the [100] axis.

2. Magnetic susceptibility

Bulk magnetic measurements were performed along the three main symmetry directions of the tetragonal unit cell. The extraction method was used in magnetic field strengths up to 8 T in the temperature range 1.5–300 K. The temperature dependence of the paramagnetic reciprocal susceptibility (figure 1) has been obtained from zero-field extrapolation of the M^2 versus H/M Arrott plots. Two characteristics are worth emphasis.

(i) In the whole temperature range, the anisotropy between the axis [001] and the basal plane is particularly huge, compared with that often observed for other $RM_2M'_2$ compounds [8], the c axis being strongly favoured. This large anisotropy is in complete agreement with the behaviour of other compounds of the series, such as $PrRu_2Si_2$ [3]. Moreover, within the basal plane, the temperature dependences of the susceptibility along the [100] and [110] axes are identical, as expected for a tetragonal compound.

(ii) The high-temperature reciprocal susceptibility seems to follow a Curie–Weiss law with an effective moment of $12.07\mu_B$, noticeably larger than the Dy^{3+} free-ion value ($10.65\mu_B$). This large difference between the theoretical slope and the experimental slope (13.3%) cannot be attributed only to the small Pauli contribution usually observed in many compounds of the $RM_2M'_2$ series but suggests that the Curie–Weiss free-ion behaviour is not yet established at 300 K as a consequence of huge crystal-field effects. The same behaviour was observed for $PrRu_2Si_2$ [3]. The temperature dependence of the paramagnetic reciprocal susceptibility shows that the crystal-field parameters responsible for those deviations play a great part in the quantitative description of $DyRu_2Si_2$. It is impossible, taking into account the previous remark, to give accurate values for B_{20} and the paramagnetic Curie temperatures.

The low-temperature variation in the magnetization along and perpendicular to the c axis is shown in figure 2, for an applied field strength of 0.2 T. Along the c easy axis, a first maximum occurs at the Néel temperature $T_N = 29.3$ K. Below 7 K, a strong increase in the magnetization can be observed when the temperature decreases, as already mentioned [7]; this was attributed to the non-compensated antiphase magnetic structure due to the particular propagation vector, which should lead to a small ferromagnetic component at low temperatures. However, a new anomaly appears at 2.2 K where a sharp maximum occurs, the decrease in magnetization observed below T_t being in apparent contradiction with the above assumption. It could be the signature of a magnetic phase transition. This point will be discussed later. The magnetization within the basal plane remains weak and no particular anomalies are detected at the ordering temperature nor below T_N.

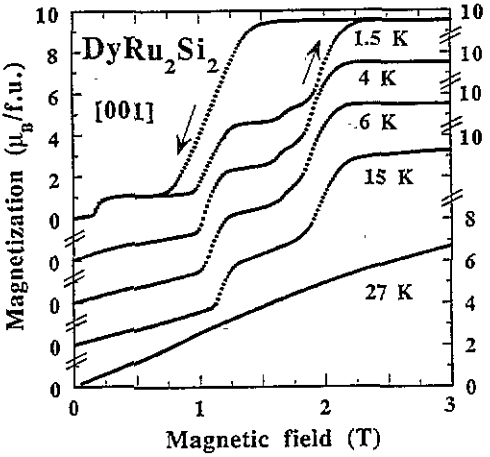

Figure 3. Magnetization curves for $DyRu_2Si_2$ at various temperatures for a magnetic field applied along the [001] easy axis.

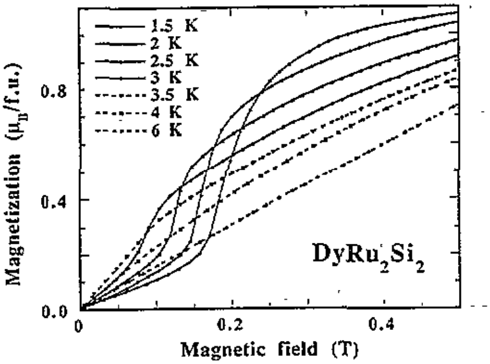

Figure 4. Low-field low-temperature magnetization curves for $DyRu_2Si_2$ along the [001] easy axis.

3. Magnetization processes

3.1. Magnetization along the [001] axis

Various isothermal magnetization curves are shown in figure 3 for a magnetic field applied along the [001] easy axis. A multistep behaviour, with a huge hysteresis for some of the transitions, is clearly observed. It is worth noting that, in an external field, the transition slope approximately coincides with the demagnetizing field slope; therefore the transitions should have a vertical slope in internal field, at least at low temperatures. However, as the demagnetizing field factor is not accurately known (the sample shape is not spherical), the results are presented in an external field. At 1.5 K, saturation is achieved above 2.3 T, the corresponding magnetization reaching $9.6\mu_B$ FU^{-1} in 7.6 T. As this value is very close to the free-ion saturated value ($10\mu_B$), the antiferromagnetic structure can be considered as completely destroyed above 2.3 T, and the crystal-field effects do not lead to a noticeable reduction in the magnetic moment along this direction. This is in agreement with previous Mössbauer experiments which have shown that the ground state is almost a pure $|\pm\frac{15}{2}\rangle$ state [7].

In an increasing field, four transitions are observed at the successive critical field strengths 0.2, 1.1, 1.7 and 2 T at 1.5 K. A huge hysteresis is observed below 10 K for the highest three transitions. During the decreasing-field process, it is worth noting that two intermediate phases vanish. The magnetization after the first transition reaches $1.1\mu_B$ FU^{-1} and this strongly supports a ferrimagnetic-like arrangement at 0 K, i.e. the magnetic structure described by an unbalanced antiphase structure due to an odd number of magnetic moments in the magnetic unit cell. This is consistent with a previous determination of the propagation vector, namely $Q = (\frac{2}{9}, 0, 0)$; indeed, the magnetization of $1.1\mu_B$ FU^{-1} corresponds nearly to a ninth of the saturated value ($M_S = 9.6\mu_B$ FU^{-1}), in agreement with a five-*up*–four-*down* moment configuration. However, at 1.5 K, the initial magnetization slope is very weak (figure 4), suggesting that the $H = 0$ magnetic phase is *not* this unbalanced antiphase structure, this latter being achieved only above the first critical field strength (0.2 T). Considering the other plateaux in the low-temperature magnetization process, it turns out that the second and third plateaux correspond roughly to $\frac{1}{2}M_S$ and $\frac{5}{9}M_S$, respectively. This latter value of $\frac{5}{9}M_S$ is consistent with a seven-*up*–two-*down* moment configuration and remains to be checked by neutron diffraction. However, the former value of $\frac{1}{2}M_S$ is not directly related to the nine-site periodicity. The explanation could be found in the double-Q character of the corresponding magnetic structure which has been recently established [9].

When the temperature is increased, all the transitions are shifted as a function of the magnetic field and smoothed off. The determination of the critical fields becomes more difficult, in particular in the vicinity of T_N. The temperature dependence of the critical fields has been extracted from the field derivatives dM/dH. The corresponding phase diagram is shown in figure 5, for an increasing field. It exhibits four distinct magnetic phases in addition to the induced ferromagnetic phase. The main magnetic phase (phase I) covers almost the full temperature range in the low-field region, in agreement with previous neutron diffraction data on powders in zero field, which indicated no change in Q in the whole ordered state. No anomaly has been detected when the M_{3Q} harmonic has been shown to appear, i.e. near 19 K. Therefore, the change from the modulated structure towards the antiphase structure is continuous. A new magnetic phase (phase II) has been established by the present study in $DyRu_2Si_2$ in the low-field low-temperature range. It is associated with the peak observed in the susceptibility variation (see section 2). It occurs below $T_t = 3.5$ K, as confirmed below by specific heat and resistivity measurements (sections 4 and 5). In high

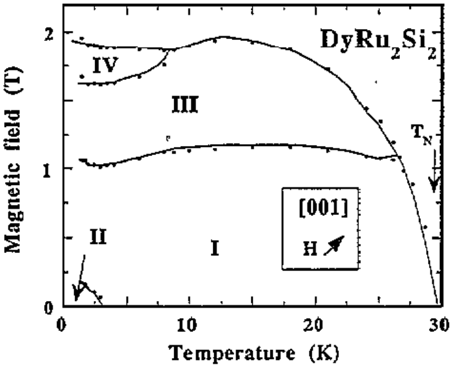

Figure 5. Magnetic H–T phase diagram for $DyRu_2Si_2$ for the [001] axis in an increasing field.

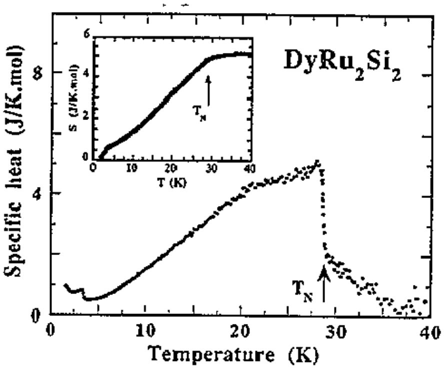

Figure 6. Magnetic contribution to the specific heat of $DyRu_2Si_2$. The inset shows the temperature dependence of the entropy.

fields a wide magnetic phase (phase III) corresponds to the double-Q structure mentioned above [9]. Finally, the highest-field magnetic phase (phase IV) had not been observed previously.

3.2. Magnetization perpendicular to the [001] axis

The behaviours of the magnetization along both directions of the basal plane, i.e. [100] and [110], are very similar. No field-induced transitions are observed, the behaviour remaining linear in the field range investigated. The magnetization along [100] reaches only $0.85\mu_B$ FU^{-1} at 2 K for an applied field strength of 7 T, a value more than ten times lower than along the [001] axis.

4. Specific heat measurements

The specific heat measurements have been carried out using the AC method, in the temperature range 1.5–40 K. The specific heat of $LaRu_2Si_2$ [10] has been used to estimate the phonon contribution. By using a many-Debye-temperature model [11], the lattice contribution to the specific heat of $DyRu_2Si_2$ has been deduced, taking into account the difference between the Dy and La molar masses. The renormalization ratio used for the Debye temperatures is 0.97.

The magnetic contribution to the specific heat of $DyRu_2Si_2$ is shown in figure 6. A well defined anomaly is observed at $T_N = 29.3$ K; it is characteristic of the appearance of the magnetic order. The jump in specific heat at T_N reaches about 5 J K^{-1} mol^{-1}. No other anomaly can be detected between T_N and about 3.6 K. However, at low temperatures an anomalous behaviour of the specific heat occurs. A detailed analysis of this low-temperature anomaly reveals two phenomena.

(i) The first is characterized by a jump of 0.3 J K^{-1} mol^{-1} at $T_t = 3.5$ K, but the shape of the peak is far from that expected for a first-order transition; a slight hysteresis of about 0.1 K has been observed;

(ii) The second feature is a regular increase in the specific heat when the temperature decreases below 2.5 K. The former anomaly is obviously associated with the magnetic phase II mentioned above (section 3). The latter could be related to hyperfine interactions. However, describing this low-temperature increase by an AT^{-2} law leads to a coefficient A of about 2.6 J K mol^{-1}, a value surprisingly high among the dysprosium compounds where A ranges rather around 0.01 J K mol^{-1} [12]. This is confirmed by calculating the hyperfine contribution itself from the hyperfine parameters determined by Mössbauer measurements [13]; this contribution actually remains below 0.1 J K^{-1} mol^{-1} at 1.6 K, ruling out definitively the hyperfine origin of this anomaly. This latter then has probably to be attributed to the 4f magnetism of $\mathrm{DyRu_2Si_2}$ and possibly connected also with the phase II.

By integrating the C–T curve, the entropy variation has been deduced (inset of figure 6). The missing entropy below 1.5 K is difficult to estimate because of the presence of the low-temperature anomalies. However, the entropy at T_N cannot be expected to be strongly modified, i.e. its value is very close to $R \ln 2 = 5.76$ J K^{-1} mol^{-1}. It follows that the crystal-field ground state is probably a doublet well isolated from the next energy levels, as previously mentioned [7]. From this result, the magnitude of the jump of specific heat at T_N can be estimated using the periodic field model, considering an isolated doublet ground state [14]. While this jump should reach 12.5 J K^{-1} mol^{-1} in the case of a simple antiferromagnetic structure, the value is reduced to 8.4 J K^{-1} mol^{-1} for a single-Q modulated structure, and to 5.5 J K^{-1} mol^{-1} for a double-Q modulated structure. Therefore this result seems to be in favour of a double-Q structure at T_N and in zero field.

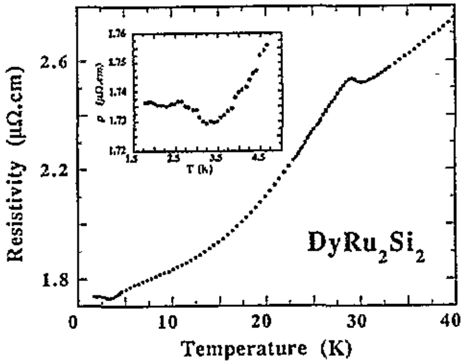

Figure 7. Temperature variation in the resistivity of $\mathrm{DyRu_2Si_2}$. The inset shows the low-temperature anomaly.

5. Resistivity measurements

The resisitivity was measured on a polycrystal by the AC four-probe method from 1.6 to 50 K. The sample, owing to its brittleness, did not have a very regular shape. The absolute value of the resistivity must then be considered as indicative. The temperature dependence of the resistivity confirms the existence of an anomaly around 3.5 K (figure 7). An increase in the resistivity when the temperature is decreased indeed occurs below this temperature. This behaviour is quite unusual for a rare-earth compound in the ordered phase. Preliminary results in the presence of a magnetic field applied parallel to the direction of current flow indicate that the anomaly vanishes above a few kilooersteds, in full agreement with the domain of existence of phase II (see section 3). However, as the resistivity is anisotropic, a detailed study on a single crystal remains to be made. A second anomaly is observed at T_N, as expected. Moreover, above T_N, a slight minimum of the resistivity occurs, as often observed for rare-earth systems where an incommensurate or long-period commensurate magnetic structure takes place at T_N [15].

6. Discussion

Extensive knowledge of the magnetic properties of the tetragonal $DyRu_2Si_2$ compound has been obtained by the present investigation. The main features are the following.

(i) The magnetic behaviour is characterized by a huge crystal-field anisotropy favouring the [001] direction. Moreover, at low temperatures, the saturated magnetic moment, i.e. the moment measured in the induced ferromagnetic state (above 2.5 T), is close to its maximum value, in agreement with a crystal-field ground state having a nearly pure $|\pm\frac{15}{2}>$ component. In addition, the behaviour of the entropy strongly suggests the existence of a doublet ground state well isolated from the excited crystal-field levels.

(ii) The magnetic structure is long period commensurate, with a propagation vector $Q = (\frac{2}{9}, 0, 0)$. This periodicity does not seem to change as a function of the temperature, according to the powder neutron diffraction [7]. This particular vector leads to a gradual evolution of the structure, from a pure sine-wave-modulated structure at $T_N = 29.3$ K to a non-compensated antiphase structure at low temperatures.

(iii) As observed for numerous other rare-earth compounds exhibiting both a long magnetic periodicity and a strong uniaxial-type symmetry, $DyRu_2Si_2$ presents, at low temperatures, magnetization processes with a multistep character, i.e. showing several sharp field-induced transitions with intermediate well defined plateaux.

(iv) This multistep behaviour allows us to define four different magnetic phases in the field–temperature phase diagram, two of which had not been discovered previously (phases II and IV). Of these, phase II appears to have a very unusual character, as shown by specific heat and resistivity measurements.

Some questions remain about the magnetic properties of this compound. The first remaining question concerns the exact nature of phase II. The temperature variation in the specific heat below 3.5 K is quite unusual, in particular if the strong increase below 2 K is considered. Indeed, a hyperfine origin for this upturn being excluded, it should be related to the magnetic phase II itself. Therefore, measuring the specific heat variation below 1.6 K appears strongly desirable. Furthermore, the resistivity variation is very unusual as well, since any magnetic transition is generally associated with a *decrease* in resistivity below the transition temperature and not an *increase*. The third anomalous behaviour of this phase II concerns the magnetization variation. According to previous powder neutron diffraction data [7], the unbalanced antiphase structure (five *up*–four *down*) seems to be achieved near 6 K. Therefore, the magnetization process should exhibit a spontaneous component of about $M_S/9$ below this temperature. On the contrary, the low-field experimental variation is still quite linear at 6 K, a behaviour which is rather the signature of an incommensurate periodicity in such a strong uniaxial system. The magnetization variation becomes a plateau only below 2 K and above the first critical field. A possible explanation could be the occurrence of a new propagation vector, possibly very close to Q, in phase II. An explanation in terms of a magnetic impurity seems to be excluded, since several different samples were involved in the different experiments, giving results consistent with each other.

Another point remaining to be solved is the single- or double-Q character of the magnetic structure according to the field and temperature. Indeed, neutron results seem to indicate a double-Q structure in phase III [9] while the specific heat variation seems to be in favour of a double-Q structure at T_N, i.e. in phase I. A detailed neutron diffraction study under a field on a single crystal is needed to elucidate the anomalous low-field low-temperature behaviour of $DyRu_2Si_2$, and to obtain complementary information about the multiple-Q character of its magnetic structure. Also, specific heat measurements below 1.6 K and resistivity measurements under a field are in progress to give us a better knowledge of this very interesting compound.

Acknowledgments

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