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Abstract

The field dependence of the magnetization in antiferromagnetic $Nd_6Fe_{13}Si$ has been measured between 4.2 and 295 K under an applied magnetic field of between zero and 23 T. Isofield magnetization measurements at 1, 10, 15 and 20 T have also been carried out between 4.2 and 295 K. The magnetic phase diagram of $Nd_6Fe_{13}Si$ contains three regions. Between 4.2 and 110 K, the magnetic moments are aligned within the basal plane of the tetragonal unit cell and two critical fields are observed. Between 160 and 295 K, the magnetic moments are aligned along the c-axis and one critical field is observed. Finally, between 110 and 160 K, a complex intermediate or mixed magnetic phase with up to three critical fields is observed. At 4.2 K and 23 T a hysteresis with a substantial coercive field of 0.4 T is observed. The presence of both two critical fields and hysteresis at low temperatures indicates a strong magnetic anisotropy within the basal plane. At 295 K an applied field of 23 T does not yield a complete spin flop of the axial magnetic moments, which remain canted. The critical field in the high temperature region is smaller than that observed in the low temperature region, indicating that the uniaxial antiferromagnetic exchange is weaker than the basal exchange. The temperature dependence of the magnetization under applied fields of 15 and 20 T shows the overall expected decrease with increasing temperature but with a break between 80 and 110 K in the spin reorientation region. Finally, the temperature dependence of the magnetization under applied fields of 10 T or less is very complex

and results from a field induced canting of the magnetic moments below 30–40 K and a minimum in magnetic anisotropy around the spin reorientation at 110 K.

1. Introduction

$Nd_6Fe_{13}Si$ crystallizes [1] in the tetragonal $I4/mcm$ space group and is antiferromagnetic with a Néel temperature of 421 K.

The complex antiferromagnetic behaviour of $Nd_6Fe_{13}Si$ has been studied [2] by means of neutron diffraction between 4 and 421 K; the crystal and magnetic structures are shown in figure 1. Between 100 and 421 K, the neodymium and iron magnetic moments are aligned parallel to the c-axis, whereas, between 4 and 100 K, they are parallel with the basal plane. Within a block delimited by the silicon atoms, the neodymium and iron magnetic moments are ferromagnetically coupled and the resulting magnetic moments of adjacent blocks along the c-axis are antiferromagnetically coupled. The spin reorientation observed by means of neutron [2] diffraction at 100 K has also been observed [3, 4] by Mössbauer spectroscopy. However, whereas the neutron diffraction measurements below 100 K are compatible with either a completely basal magnetization or a mixture of 25% of axial and 75% of basal magnetization, the Mössbauer spectral measurements are only compatible with a mixture of 25% axial and 75% basal magnetization. This surprising observation was attributed to the presence of about 8% of an $Nd_2Fe_{17-x}Si_x$ impurity.

There have been earlier partial applied field studies [1, 5, 6] but they could not be analysed in detail because the complex antiferromagnetic structure [2] of $Nd_6Fe_{13}Si$ was unknown at the time. Above 225 K Yan *et al* [5] observed one critical field of about 5.3 T, whereas below 225 K they observed two critical fields of 6.2 and 8.2 T. Further, these authors observed a minimum critical field of 3.4 T at 180 K. Unfortunately, they could not interpret these results in view of the incorrect antiferromagnetic structure they had derived from low resolution neutron diffraction patterns. Subsequently, de Groot *et al* [1] observed a two-step magnetization curve up to 27 T, with critical fields of 7.8 and above 20 T. More recently, Ruzitschka *et al* [6] observed a two-step magnetization curve at 4.2 K with critical fields of 7 and 11 T; at 150 K they observed a broad transition in the magnetization.

The goal of the present study is to understand in detail the behaviour of the spin reorientation in $Nd_6Fe_{13}Si$ in the presence of large applied magnetic fields. More specifically, the goal is to determine the relationship between the critical fields and the spin reorientation. A good understanding of this relationship is important because both $Nd_2Fe_{17-x}Si_x$ and $Nd_6Fe_{13}Si$ are present in the neodymium, iron and silicon ternary phase diagram and both compounds play an important role in determining the magnetic properties of hard magnetic materials derived from neodymium, iron and silicon.

2. Experimental details

The sample of $Nd_6Fe_{13}Si$ used herein is the same as that used in our earlier studies [1–4]. Its purity and crystallographic structure have been discussed in detail in [2].

The magnetization of $Nd_6Fe_{13}Si$ was measured between 4.2 and 295 K in applied fields of zero to 23 T at the Laboratoire des Champs Magnétiques Intenses in Grenoble, France. Isofield measurements at 1, 10, 15 and 20 T were also carried out between 4.2 and 295 K. The samples studied were prepared from powder with an average particle size of about 50 μm.
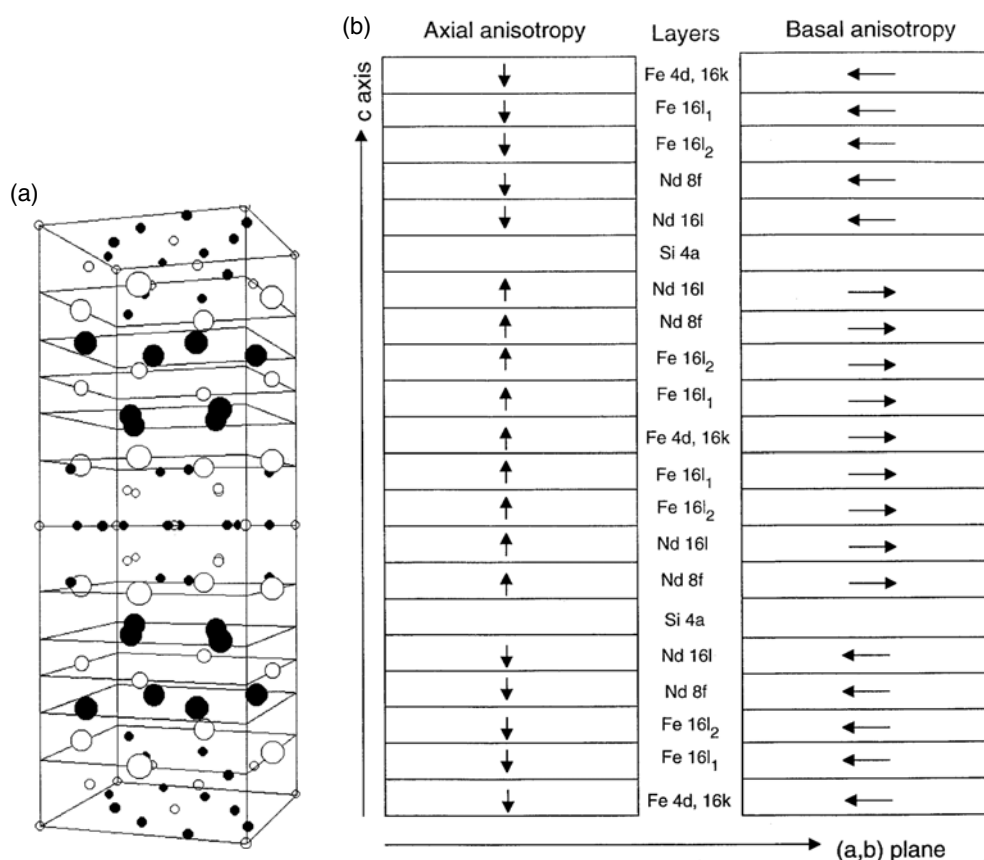
Figure 1. (a) The crystal structure of $Nd_6Fe_{13}Si$ where the large black and white atoms are neodymium 16l and 8f, the intermediate size white atoms are silicon 4a, the small black atoms are iron 16k and $16l_2$, and the small white atoms are iron 4d and $16l_1$. The layers containing the neodymium 8f, neodymium 16l and silicon 4a sites are delineated. (b) A schematic diagram of the magnetic structure of $Nd_6Fe_{13}Si$ at high temperature, left, and low temperature, right.

The powder was pressed tightly into a container in order to avoid rotation of the grains during the application of the high magnetic field. The absence of rotation is confirmed by the quasi-perfect agreement between the magnetization values obtained in the isothermal and isofield measurements. The magnetic measurements were performed using an automatic system [7] equipped with a cryostat associated with a calorimeter.

3. Experimental results

The field dependence of the magnetization per formula unit observed for $Nd_6Fe_{13}Si$ at 4.2, 100, 110, 130, 150 and 280 K is shown in figure 2 and the corresponding derivative, $(dM/dH)_T$, is shown in figure 3. Additional measurements, not shown in figures 2 and 3, have been carried out at the additional temperatures indicated in figure 4.

As is most easily seen in figure 3 at 4.2, 100 and 110 K, between 4.2 and 110 K two peaks, H_1 and H_2, are observed in the derivative of the magnetization. Thus, between 4.2 and 110 K two critical fields are observed; see figure 4. In contrast, above 122 K the magnetization
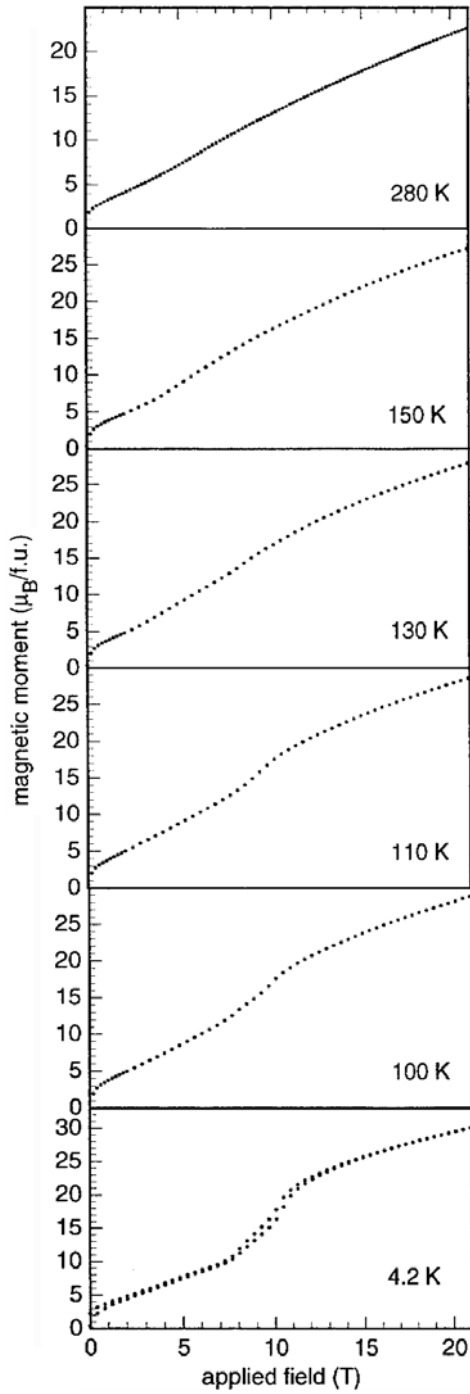
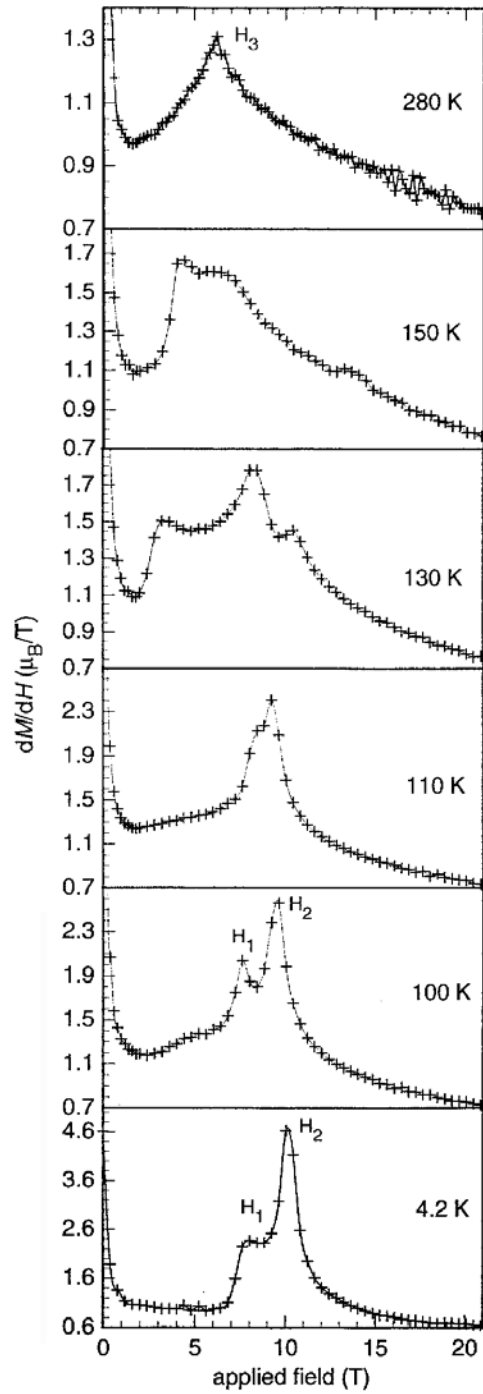**Figure 2.** The field dependence of the magnetization per formula unit of $Nd_6Fe_{13}Si$ observed at the indicated temperatures.

Figure 3. The field dependence of the derivative of the magnetization, $(dM/dH)_T$, per formula unit of $Nd_6Fe_{13}Si$ observed at the indicated temperatures.
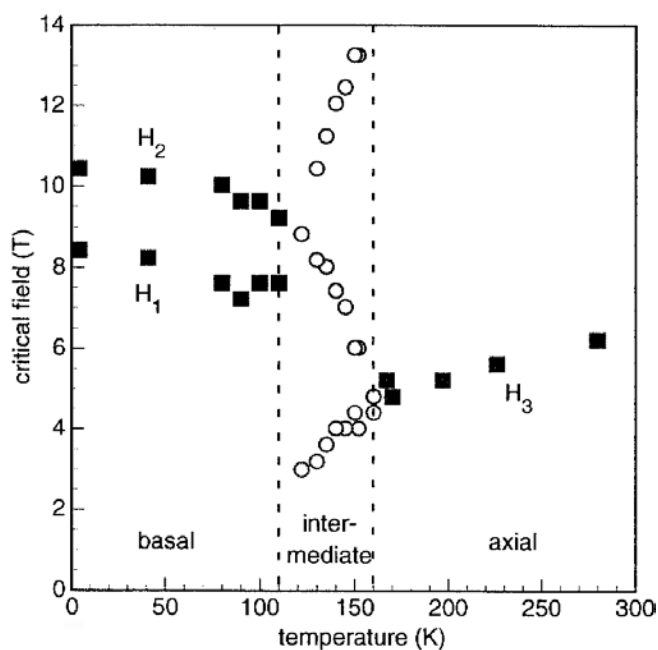
Figure 4. The temperature dependence of the critical fields observed in $Nd_6Fe_{13}Si$.

increases rather uniformly with applied field; see the 130–280 K results in figure 2. However, the derivative curves shown in figure 3 reveal a more complex behaviour above 122 K. Although at 122 K only one critical field is observed, between 130 and 152 K three critical fields are observed in the $(dM/dH)_T$ plots. Finally, above 160 K only a single peak at H_3, and thus one critical field, is observed. The critical fields obtained with increasing applied field are shown as a function of temperature in figure 4.

It is clear from figure 4 that the magnetic phase diagram of $Nd_6Fe_{13}Si$ has three main regions, with differing critical fields, regions which correspond to the axial, intermediate or mixed and basal orientations of the iron and neodymium magnetic moments as observed [2–4] by means of both neutron diffraction and Mössbauer spectroscopy.

In agreement with previous measurements [1, 6], two critical fields are observed at 4.2 K in $Nd_6Fe_{13}Si$. However, the observed fields of 8.4 and 10.4 T are higher than those reported earlier [1, 6]. In a similar fashion, the two critical fields observed below 122 K are larger than the 6.2 and 8.2 T fields previously observed [5] below 225 K. Further, in contrast to the previous report [5], no real minimum critical field is observed herein at 180 K. In contrast, above 160 K, the single critical fields of 5–6.2 T agree well with the previous measurements [5] above 225 K. Hence, the results presented herein are in approximate agreement with the earlier results but the critical fields and critical temperatures vary somewhat.

Because both the neutron diffraction and the Mössbauer spectral results [2–4] on $Nd_6Fe_{13}Si$ have revealed the presence of about 8% of a Nd_2Fe_{17} impurity in the sample under study herein, it is important to determine whether or not the observed magnetization curves shown in figure 2 and the critical fields given in figure 4 are strongly influenced by the presence of this impurity. Indeed, it is worth noticing that an earlier 4.2 K high field magnetization study [8] of a Nd_2Fe_{17} single crystal indicates the presence of a major increase at 10 T and a minor increase at 18 T in the magnetization along the c-axis, the hard magnetic

axis. Thus the 4.2 K measurements on $Nd_6Fe_{13}Si$ have been corrected for the presence of 8% of Nd_2Fe_{17} by using the previously published [9] 4.2 K magnetic data. This correction, as expected for antiferromagnetic $Nd_6Fe_{13}Si$, yields zero magnetization at 4.2 K at zero applied field. However, the correction does not change the shape of the two steps in the magnetization curve or its derivative curve and, further, the correction only reduces the two critical fields by 0.4 T, an approximately 5% change in the critical field.

4. Interpretation and discussion of the results

First, it is important to note that at 4.2 K and 23 T the magnetization of $Nd_6Fe_{13}Si$ is at most 30 μ_B per formula unit, a value that is substantially smaller than the 46.2 μ_B per formula unit value expected for the ferromagnetic alignment of all the neodymium and iron magnetic moments in $Nd_6Fe_{13}Si$. Hence, the antiferromagnetic exchange coupling in $Nd_6Fe_{13}Si$ is very strong and, even in a field of 23 T, the magnetic moments remain partly canted. Second, at 4.2 K there is a hysteresis in the magnetization with a substantial coercive field of about 0.4 T. In antiferromagnetic heavy rare-earth iron compounds a small hysteresis in the moment is expected [1] to arise from the magnetocrystalline anisotropy. In contrast, in antiferromagnetic lighter rare-earth iron compounds, a much larger hysteresis is expected [1] and is observed herein. As is shown by the anisotropy model of de Groot *et al* [1], the substantial 0.4 T hysteresis observed at 4.2 K in the magnetization of $Nd_6Fe_{13}Si$, when the two sublattices have planar anisotropy, indicates that there is a strong anisotropy within the basal plane. Between 4.2 and 110 K, a two-step change in the magnetization of $Nd_6Fe_{13}Si$ with two critical fields is observed. Earlier, de Groot *et al* [1] showed that such a change, at least for the case of a free powder, can be understood in terms of a simple approach that minimizes the local energy in a two-sublattice model. In the present case, at these temperatures, the two sublattices [2] are the two antiferromagnetically coupled ferromagnetic blocks, blocks that have the same magnetization and basal anisotropy, as is shown in figure 1(b). Further, the large hysteresis observed for a magnetic structure in which the two sublattices have planar anisotropy indicates [1] that there is a strong anisotropy within the basal plane. In addition, the presence of two critical fields in this region may be related to the existence of an anisotropy within the basal plane.

In polycrystalline $Nd_6Fe_{13}Si$ above 160 K, as the applied field increases, depending upon the orientation of the easy *c*-axis of an individual crystallite relative to the field, the antiferromagnetically coupled spins will either undergo a spin-flop transition at a critical field followed at higher applied fields by a canting in the direction of the applied field or gradually cant in the direction of the applied field. However, ferromagnetic alignment is not achieved even at 23 T, as is indicated by the absence of saturation of the magnetization in figure 2. The critical field observed from 160 to 295 K is smaller than the fields observed below 110 K; see figure 4. If the critical field is interpreted as the field required to overcome the antiferromagnetic coupling, these smaller critical fields indicate that the antiferromagnetic exchange energy is smaller in the axial than in the basal magnetic phase of $Nd_6Fe_{13}Si$.

In the intermediate region, between 110 and 160 K, the complex behaviour of $Nd_6Fe_{13}Si$ with applied field is clearly related to the presence of either mixed magnetic phases or an intermediate magnetic phase with a large canting of the moments from the *c*-axis. Unfortunately, the origin of the three critical fields is less than obvious.

The temperature dependence of the maximum in the derivative of the magnetization, dM/dH, observed in $Nd_6Fe_{13}Si$, calculated at the critical fields indicated in figure 3, is shown in figure 5. A dramatic decrease in $(dM/dH)_{H_2}$ is observed between 4 and 110 K, a decrease which reflects the smoothing of the field induced transition in the magnetization with increasing temperature; see figure 2. In comparison, $(dM/dH)_{H_1}$ decreases only slightly between 4 and
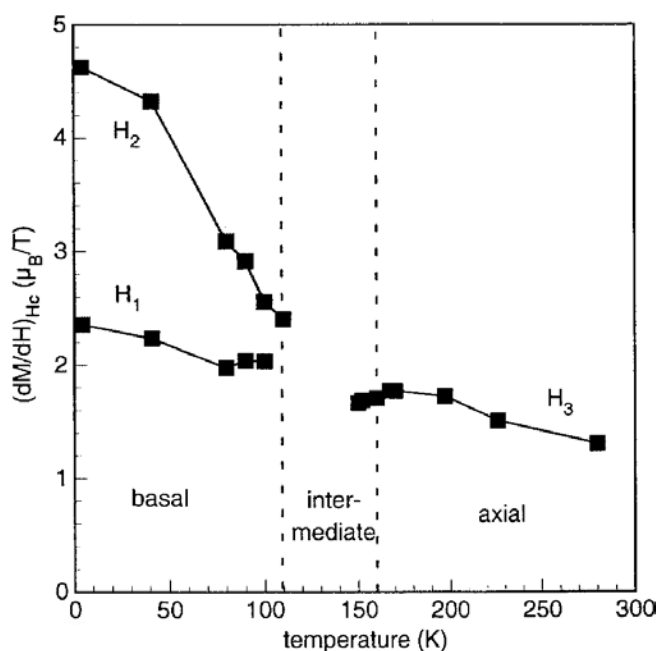
Figure 5. The temperature dependence of the maximum in the derivative of the magnetization of $Nd_6Fe_{13}Si$ obtained at the critical fields.

110 K. In contrast, $(dM/dH)_{H_3}$ is virtually independent of temperature, an independence which indicates that the ability of the magnetization to follow the applied field is essentially constant between 160 and 295 K.

The temperature dependence of the magnetization in applied fields of 1–20 T is shown in figure 6. For applied fields of 15 and 20 T, the magnetization decreases with increasing temperature in a rather usual fashion except for a break between 80 and 110 K, a break which is reminiscent of the changes [2] in the neodymium and iron magnetic moments at the spin reorientation in zero applied field. At 15 and 20 T, the magnetic moments have undergone the near spin flop described above and yield a large magnetization of about 30 μ_B per formula unit. As the temperature increases above 4.2 K, the magnetization first decreases. Then, as the temperature reaches 80 K, the magnetic anisotropy competes with the thermal energy and the canting angle between the magnetic moments and the field changes. This competition is likely to give rise to the break in the temperature dependence of the magnetization. When the temperature increases above the spin reorientation temperature, the uniaxial character of the magnetic anisotropy increases and hence perturbs the alignment of the magnetic moments in the field. The combination of this perturbation and the normal decrease in the magnetic moments with increasing temperature leads to the decrease in magnetization observed at 15 and 20 T above 110 K.

At 1, 5 and 10 T, the magnetization exhibits a minimum at about 30–40 K and a rather broad maximum between 80 and 110 K, i.e., at the spin reorientation temperature. A similar behaviour was observed [10] for $Pr_6Fe_{13}Sn$ in applied fields of between 0.05 and 5 T. The origin of the decrease between 4 and 30–40 K has been attributed [10] to a field induced canting of the magnetic moments of the different sublattices. Because at the spin reorientation transition the basal and axial magnetic anisotropies cancel each other, the total magnetic anisotropy is
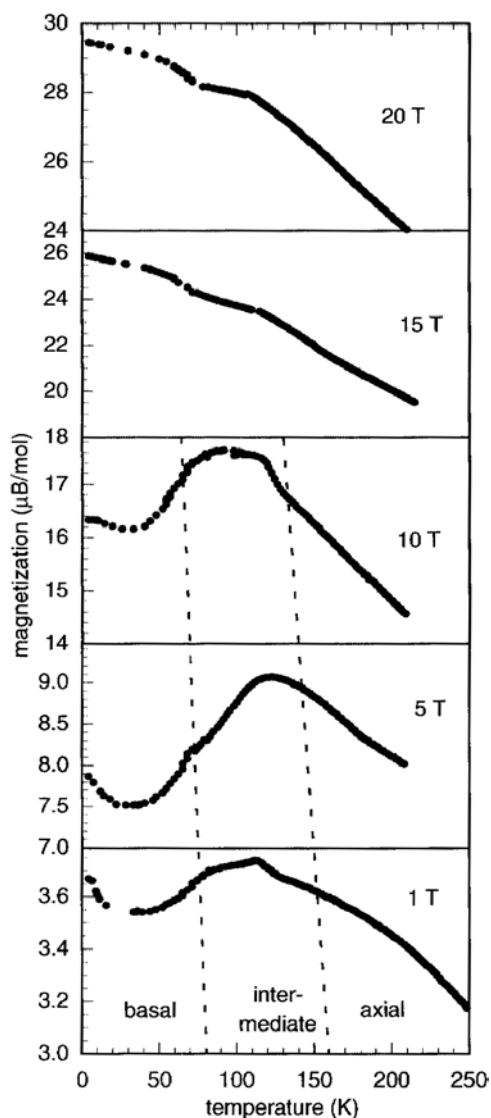
Figure 6. The temperature dependence of the magnetization per formula unit of $Nd_6Fe_{13}Si$ obtained at the indicated applied fields.

essentially zero and the magnetic moments cant more easily in the applied field to give rise to a maximum in the magnetization. Because the spin reorientation occurs over a temperature range of about 30 K at zero applied field [3, 4], this maximum is broad at 1, 5 and 10 T. Further, its shape and position show a field dependence that indicates that the spin reorientation transition temperature range is a function of the applied field.

5. Conclusions

Similar spin reorientations have been observed [2, 11] by means of neutron diffraction in both $Nd_6Fe_{13}Si$ and $Nd_6Fe_{13}Ga$. Unfortunately, the magnetic properties of $Nd_6Fe_{13}Ga$ could not

be investigated in detail because of the presence of a significant amount of the ferromagnetic Nd$_2$Fe$_{17}$ impurity, even more than the 8% found in the Nd$_6$Fe$_{13}$Si sample studied herein. In both compounds, above 100 K, the magnetic moments are parallel to the c-axis. Below 100 K they are aligned in the basal plane in Nd$_6$Fe$_{13}$Si and cant by an undetermined angle, ϕ, away from the c-axis in Nd$_6$Fe$_{13}$Ga. In Nd$_6$Fe$_{13}$Ga, this spin reorientation was explained [11] as resulting from the competing anisotropies of the two rare-earth and four iron sublattices. Because of the similar crystallographic and magnetic structures of Nd$_6$Fe$_{13}$Si and Nd$_6$Fe$_{13}$Ga, it is reasonable to conclude that the spin reorientation in Nd$_6$Fe$_{13}$Si has the same origin. At higher temperatures, the magnetic anisotropy is governed by the second-order crystal-field terms and, thus, the magnetic anisotropy is essentially dominated by the iron anisotropy constant, an anisotropy that favours an axial orientation of the magnetic moments. As the temperature decreases, the anisotropy of the two neodymium sites increases but the sites have opposite sign anisotropy constants and, hence, virtually compensate each other. However, with further temperature decreases, the two neodymium site fourth-order crystal-field terms contribute a positive term to the anisotropy energy which leads [11] to an increase of up to 90° in the canting angle, ϕ. Because of the large magnetostriction observed [2] in Nd$_6$Fe$_{13}$Si at the spin reorientation, a substantial change in these two fourth-order crystal-field parameters is quite likely and a subsequent rapid increase with decreasing temperature in the fourth-order contribution to the magnetic anisotropy induces the spin reorientation below 110 K.

In conclusion, it seems that the shape of the curves in figures 2 and 6 results from a complex interplay between the anisotropies of the two neodymium sublattices and the four iron sublattices, their temperature dependences and the sensitivity to the applied field of the antiferromagnetic exchange.

Acknowledgments

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