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Abstract

We have grown single crystals of $YbFe_6Ge_6$ and $LuFe_6Ge_6$ and characterized their anisotropic behaviour through low-field magnetic susceptibility, field-dependent magnetization, resistivity and heat capacity measurements. The Yb^{3+} valency is confirmed by L_{III} XANES measurements. $YbFe_6Ge_6$ crystals exhibit a field-dependent, sudden reorientation of the Fe spins at about 63 K, a unique effect in the RFe_6Ge_6 family (R = rare earths), where the Fe ions order anti-ferromagnetically with Neél temperatures above 450 K and the R ions' magnetism appears to behave independently. The possible origins of this unusual behaviour of the ordered Fe moments in this compound are discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The combination of localized 4f-electron magnetism with delocalized 3d-electron or band magnetism can often provide both interesting physical phenomena from the academic perspective, and potentially useful effects from the application perspective, thus making it a continuous topic of interest in materials science and magnetism. To study the coexistence and relationships between these different types of magnetic entities in the same compound, one will usually focus on binary or ternary intermetallics containing both rare-earth elements (Ce–Yb) and 3d-shell transition metals Mn–Ni.

RT_6X_6 (R = rare earths; T = Mn, Fe, Co; X = Ge, Sn) is one such family of intermetallics that has been known for several decades, and many new members of the family have been synthesized and explored extensively over the past decade or so [1, 2]. Its formation can be viewed as an insertion of R atoms into the layered, hexagonal FeGe-type binary structure (figure 1). In the ideal arrangement, R atoms alternate between complete occupation of an interstitial layer between two hexagonal Fe grids, and no occupation of the adjacent interstitial
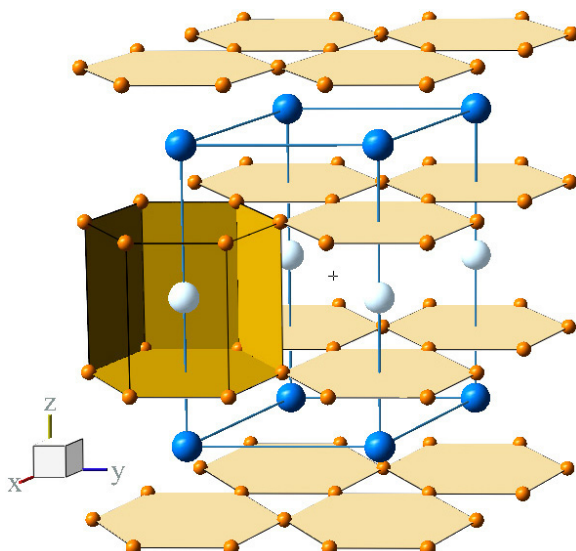
Figure 1. Schematic representation of the $HfFe_6Ge_6$-type structure ($P6/mmm$ space group). Small spheres are the Fe 6i sites, large light spheres are the Hf atom's ideally occupied 1b sites and large dark spheres are the ideally unoccupied 1a sites. The three Ge sites have been left out for clarity: they form hexagonal bipyramid Ge_8 cages around unoccupied Hf sites, or a simple co-planar hexagonal grid around occupied Hf sites. The eight unoccupied Hf sites delimit the structure's unit cell.

layers, so that the unit cell is doubled along the *c*-axis with respect to the original FeGe structure. This is known as the $HfFe_6Ge_6$-type structure, adopted by most of the RMn_6Ge_6 compounds, but only achievable by the smallest of the R ions such as Lu and Yb in the RFe_6Ge_6 series [1, 3]. In actual samples, all interstitial layers tend to become partially occupied, sometimes in a disordered version of the alternating layer structure for the smaller R ions [4], and sometimes in organized manners which lead to different symmetries and sizes of the unit cell for larger R ions [1]. Thus, the compounds in this family are intrinsically prone to disorder as one might expect, which often leads to batch and thermal history dependences of a sample's structure and properties [2, 5, 6].

Whatever the case, a crucial feature of these structures is that the R atoms always position themselves in the centre of a hexagonal prism formed by 12 T atoms (highlighted in figure 1). In most of the RMn_6Sn_6 compounds, the Mn ions order ferromagnetically at temperatures between 350 and 450 K. The 12 Mn moments in the hexagonal prism and the R magnetic moment in its centre interact strongly, with negative exchange coefficient, and the R sub-lattice was found to order simultaneously with the Mn sub-lattice, forming a ferrimagnetic structure in the material [7, 8]. In the RMn_6Ge_6 series, a set of complex ferro-, ferri- and antiferromagnetic arrangements including multiple wavevectors and transitions have been observed [1, 9–14].

In the RFe_6Ge_6 series, the Fe ions retain much of their magnetic behaviour from the parent FeGe compound. At temperatures varying between 450 and 480 K [1, 2], they order ferromagnetically and axially within a single hexagonal layer, but neighbouring Fe layers order antiferromagnetically, and thus the material assumes a simple $+ - + -$ stacking of spins along the *c*-axis. As a consequence, the net local field at the R site due to its 12 Fe neighbours of the hexagonal prism is null, and it has been found that the rare-earth sub-lattice does not order together with the Fe sub-lattice, but rather behaves quite independently [15]—ordering
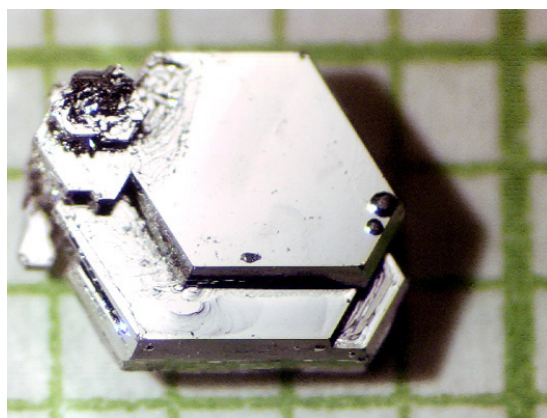
Figure 2. As-grown single crystal of LuFe$_6$Ge$_6$ on a millimetre paper. The rounded droplet-like features located at 4:00 and 10:00 are solidified Sn flux.

at much lower temperatures in some cases, or remaining paramagnetic down to the lowest measured temperatures in others. These cases were also observed in a few of the manganese based compounds where antiferromagnetic ordering of the Mn ions occurs [8].

YbFe$_6$Ge$_6$ has been reported to exhibit antiferromagnetism of the kind described above [1, 15]. Lattice parameters indicated that the Yb ion should be in or close to its 3+ state (and therefore magnetic) but remains paramagnetic down to 1.5 K. However, a neutron diffraction and Mössbauer study of polycrystalline samples by Mazet and Malaman [16] showed evidence of a spin reorientation effect where at least part of the Fe spins in their samples deviated from the c-axis below about 85 K, assuming a direction close to the basal plane. Such reorientation processes of the ordered 3d spins at intermediate temperatures have been well documented in some of the RMn$_6$Sn$_6$ compounds [17], and in this series it has been proposed that the effect results from the interplay between two competing energies: the Mn ferromagnetic interaction which dominates the high temperature region and favours an easy-plane arrangement, and the rare earths' crystal field anisotropy which becomes dominant at lower temperatures, forcing the R spins towards the c-axis and the Mn spins to shift simultaneously, due to the strong R–Mn interaction [17].

However, such a drastic spin reorientation effect is not to be expected in the 'independent sub-lattices' scenario of the RFe$_6$Ge$_6$ series, and indeed it has not been found in other members of the series. We were thus motivated by this puzzling behaviour of YbFe$_6$Ge$_6$ to address the issue by growing single crystals in order to study the material's anisotropic behaviour directly. In this work we present further evidence of this spin reorientation process in our single crystals, and discuss the possible mechanisms that may be responsible for its unique occurrence in the RFe$_6$Ge$_6$ series.

2. Experimental details

Single crystals of YbFe$_6$Ge$_6$ and LuFe$_6$Ge$_6$ were grown using Sn as a fourth-element flux [18]. Due to the relevance of thermal history previously mentioned, we wish to provide a description of our growth procedures in detail.

For LuFe$_6$Ge$_6$, thick hexagonal crystal plates weighing up to 16.5 mg (figure 2) were obtained by mixing high-purity starting elements (99.95% or better) with a Lu:Fe:Ge:Sn
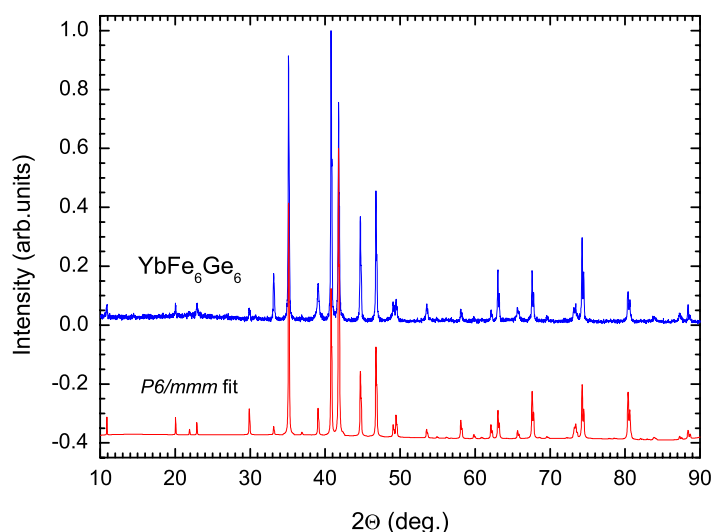
Figure 3. Powder x-ray diffraction pattern of crushed YbFe$_6$Ge$_6$ crystals and corresponding refinement.

proportion of 1:6:6:20 in an alumina crucible, which was then sealed under partial argon atmosphere inside a quartz ampoule. The ampoule was placed in a box furnace, heated to 1200 °C and maintained for 2 h, then cooled over several days to 500 °C, at which point the ampoule was quickly removed from the furnace and the molten Sn flux was separated by decanting. The decanted flux as well as most of the as-grown crystals reacted to the presence of magnets at room temperature, indicating that a ferromagnetic second phase also precipitated out of the Sn flux during the cooling process (probably an Fe-rich alloy since Fe is not very soluble in Sn) so the crystals were placed in a bath of 50% HCl in water for several days to remove any surface-attached second phase (the RFe$_6$Ge$_6$ crystals are stable even in concentrated HCl). Any crystals that still reacted to magnets after this treatment were discarded since the remaining second phase is trapped inside the crystal and is unreachable by the acid.

YbFe$_6$Ge$_6$ single crystals were somewhat more difficult to grow. Applying the same procedure as described above results in very small and thin (sub-milligram) hexagonal plates. However, this has proved to be the only phase that crystallizes over a wide range of Yb:Fe:Ge starting proportions dissolved in Sn, so this feature could be explored to our advantage. We were able to increase the crystal sizes up to 4.5 mg in a growth where an iron-deficient starting mixture was used (Yb:Fe:Ge:Sn proportion of 1:1:3:20) directly in the quartz ampoule, a soaking time of 10 h at 1200 °C and cooling to 500 °C over 4 days. Some small volume crystals grew as thin, elongated plates exceeding 2 mm in length along an *a*-axis, which were ideal for the four-probe resistivity measurements. We could also grow elongated rods along the *c*-axis instead of plates in a batch using a 1:3:6:40 starting proportion and cooling over 4 days from 800 to 600 °C. None of these crystals reacted to magnets at room temperature, but were still cleaned in HCl baths to remove any remaining flux droplets from the surface.

The phases were checked by powder x-ray diffraction on crushed crystals. Figure 3 shows the measured pattern of YbFe$_6$Ge$_6$ and its corresponding *P6/mmm* refinement, which results in cell parameters $a = 5.102(1)$ Å and $c = 8.099(1)$ Å, in good agreement with the available crystallographic data [1].
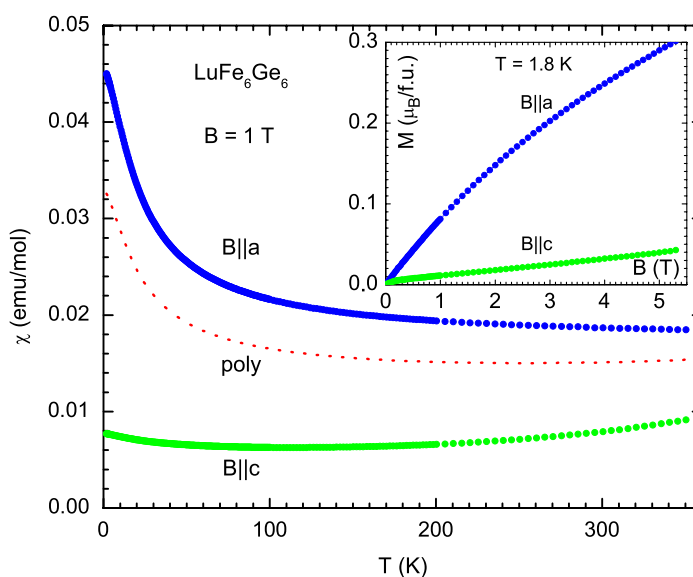
Figure 4. Anisotropic susceptibility at $B = 1$ T of LuFe$_6$Ge$_6$ in the AFM state. Inset: magnetization isotherms up to 5 T at $T = 1.8$ K.

Resistivity was measured on a home-made dc system and on Quantum Design PPMS systems. The latter were also used to perform heat capacity experiments. DC magnetization measurements were performed on Quantum Design MPMS magnetometers. Ytterbium L$_{III}$-edge XANES was measured at beamline BL01B1 of SPring-8, Hyogo, Japan. A Si(111) double-crystal monochromator with two mirrors was used to obtain the incident x-rays. XANES spectra were measured in fluorescence mode using a Lytle detector for the powdered samples at Yb 1.0 wt% diluted by boron nitride. Energy calibration was conducted by defining the peak energy of the white line for Yb$_2$O$_3$ at 8.9245 keV. The absorption of the spectra was normalized to the average absorption between 8.98 and 9.00 keV.

3. Experimental results

For comparative purposes, it is useful to initially focus on the anisotropic behaviour of LuFe$_6$Ge$_6$, where the closed electronic 4f shell of the Lu^{3+} ion does not contribute to the magnetic behaviour. Previous studies on polycrystalline samples (and several others with non-magnetic R elements) have shown AFM transitions above 450 K [17], but the simple AF arrangement of the Fe spins was found to become unstable at lower temperatures, such that at least part of the Fe spins no longer stay completely aligned with the c-axis [17, 19]. This so-called 'spin-disorientation' effect [17] is manifest in magnetic measurements as a return to an increasing susceptibility regime as the temperature is lowered, contrary to the expected behaviour of a material in the AFM state.

Although our experimental system does not reach the temperature range of the AFM transition, the measurements we have made below 350 K on a LuFe$_6$Ge$_6$ single crystal (after cleaning) supports this scenario. Figure 4 shows that the magnetic susceptibility within the AFM state is anisotropic and much larger for $B \parallel a$ than for $B \parallel c$. The $B \parallel c$ curve shows a broad local minimum at about 120 K, close to the region where deviations from axial arrangement are reported to begin [17].

It is also worth noting that the lowest temperature susceptibility is non-Curie–Weiss-like and tends towards ending in a cusp or saturation. The increase observed for $B \parallel a$ is quite strong and, by forcing a Curie–Weiss fit in the polycrystalline average curve below 100 K, we find that it would require a contamination of the order of 8% Tb (for example) to produce a comparable anisotropic increase, indicating that the observed upturn is more likely attributable to intrinsic behaviour than to impurities. The reversible magnetization curves shown in the inset of figure 4 also reveal no significant ferromagnetic component that could arise from impurity phases.

To our knowledge, no magnetization measurements on any type of $YbFe_6Ge_6$ sample have been reported so far. The orientation dependent measurements we have performed below 350 K on our single crystals gave results generally similar to that of $LuFe_6Ge_6$ until about 63 K, at which point a sudden and drastic anomaly in behaviour takes place. Figure 5(a) shows the curves for an applied field of 0.1 T. The $B \parallel c$ susceptibility increases rapidly while the $B \parallel a$ susceptibility decreases half as much, in such a way that the material's anisotropy seems to be almost completely inverted. The polycrystalline average (dotted line) estimated from these two measurements as $\chi_p = (\chi_c + 2\chi_a)/3$ remains smooth and virtually unaffected, so low-field magnetization measurements on polycrystals may indeed not reveal any hint that such a transition is taking place. It is interesting to note that there is no clear manifestation of Yb^{3+} paramagnetism in these measurements.

The anomalous behaviour is field sensitive and evolves quite differently in each orientation. For $B \parallel c$ (right inset of figure 5(b)), higher fields favour the transition, moving it to higher temperatures. Defining T_{SR} as the point where the mid-transition (highest-slope) extrapolation meets the above-transition (baseline) extrapolation, we see T_{SR} increasing from 64.0 K at 1 T to 74.3 K at 5 T. The curve shape, however, remains essentially the same in this field interval. For $B \parallel a$, by contrast, higher fields clearly act towards suppressing the transition, both in terms of moving T_{SR} to slightly lower temperatures, and in terms of decreasing the magnitude of the susceptibility change, until it has almost vanished at 5 T. This field dependence is consistent with simple energetics: high fields stabilize the high-magnetization phase and suppress the low-magnetization phase. Because of this difference, polycrystalline average curves estimated for these high-field measurements are no longer smooth and featureless as those for low fields, so the transition in magnetization should also become quite evident in powders and sintered samples measured at high enough fields.

The main graph in figure 5(b) shows a tentative phase diagram for how T_{SR} evolves with field in both orientations. Measurements made at low fields showed that T_{SR} values in both directions essentially coincide at 63.3 K for this sample. However, earlier batches showed quite different values of T_{SR} (as low as 44 K) and multiple transitions, pointing to the relevance of disorder and thermal history in this system, which will be discussed later.

Having documented the magnetic behaviour, we now present a few other experimental techniques that provide further characterization of the compound and information about the nature of the observed transition. Figure 6 shows resistivity measurements performed on an a-axis elongated $YbFe_6Ge_6$ crystal. Room temperature resistivity is about 250 $\mu\Omega$ cm, decreasing to 31 $\mu\Omega$ cm at the lowest measured temperature and resulting in RRR $= \rho(300\,K)/\rho(0) = 8.1$, a surprisingly high value for a compound that is so prone to disorder. A measurement on a $LuFe_6Ge_6$ crystal cut into bar shape is also shown, although only qualitative comparison in transport properties can be made.

Only a very subtle change in the resistivity behaviour (and thus scattering regime) of $YbFe_6Ge_6$ was found in this measurement, observable as a peak that barely rises above noise level in the derivative $d\rho/dT$ (the arrow marks T_{SR} as observed by magnetization of the same sample). This minor change gives qualitative support to the fact that the transition involves
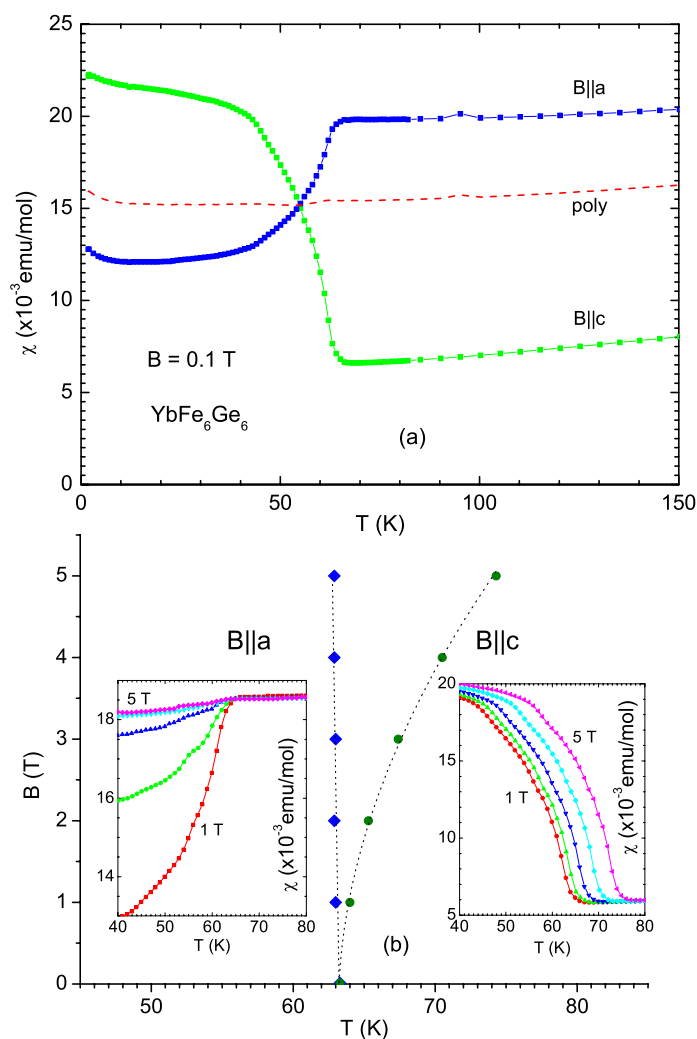
Figure 5. Low-temperature magnetic behaviour of YbFe$_6$Ge$_6$. (a) Anisotropic susceptibility at $B = 0.1$ T, showing the anomalous transition around 63 K. The dotted line is the polycrystalline average. (b) Field dependence of the transition temperature T_{SR} for both orientations. The dotted lines are guides to the eyes. The left and right insets show how the transitions evolve under applied fields of 1, 2, 3, 4, and 5 T, for $B \parallel a$ and $B \parallel c$ respectively.

a spin reorientation, and not a more fundamental structural or magnetic phase transition in the sample, in which cases much more pronounced changes in the scattering regime are usually expected. Small features in resistivity like this were also observed in the reorientation transitions of some RMn$_6$Ge$_6$ compounds [20].

Another useful measurement to help understand magnetic behaviours and/or the nature of phase transitions is the temperature-dependent heat capacity. In figure 7 we show the zero-field specific heat of both YbFe$_6$Ge$_6$ and LuFe$_6$Ge$_6$. The behaviour of both compounds is very similar, even at the lowest measured temperatures (inset), indicating that no major or drastic changes in entropy take place in YbFe$_6$Ge$_6$ in this temperature interval, compared to LuFe$_6$Ge$_6$. It is possible though that more careful measurements in the region of interest
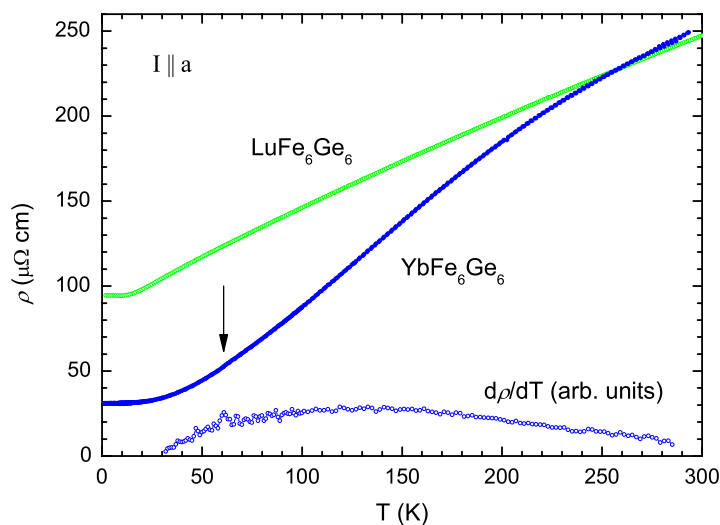
Figure 6. In-plane electrical resistivity $\rho(T)$ of $YbFe_6Ge_6$ and $LuFe_6Ge_6$ below room temperature. The derivative $d\rho/dT$ for the former is also shown.
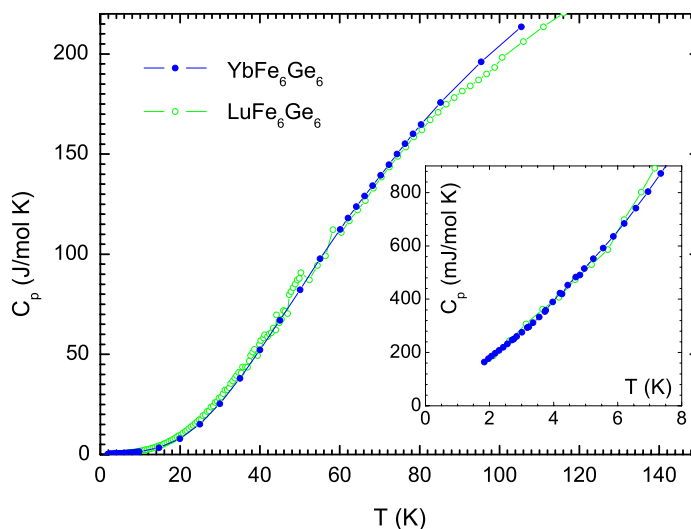

Figure 7. Zero-field specific heat of $YbFe_6Ge_6$ and $LuFe_6Ge_6$ below 100 K. The inset shows the similarity in behaviour persists down to the lowest measured temperature of 1.8 K.

could reveal some subtle features such as the one found in resistivity. The Sommerfeld coefficient estimated by extrapolating Cp/T versus T^2 to $T = 0$ is about 90 mJ mol^{-1} K^{-1} for both samples. The coincidence in behaviour of both compounds indicates that any Yb sub-lattice magnetism contributes very little to the overall entropy, and therefore the behaviour is essentially dominated by the Fe magnetism plus the electronic and lattice contributions. In fact, these results plus the apparent lack of response of the Yb ion in magnetic measurements (figure 5) raised the question of whether the Yb ion was magnetic at all, despite the indirect indication of such from the material's lattice parameters [1].
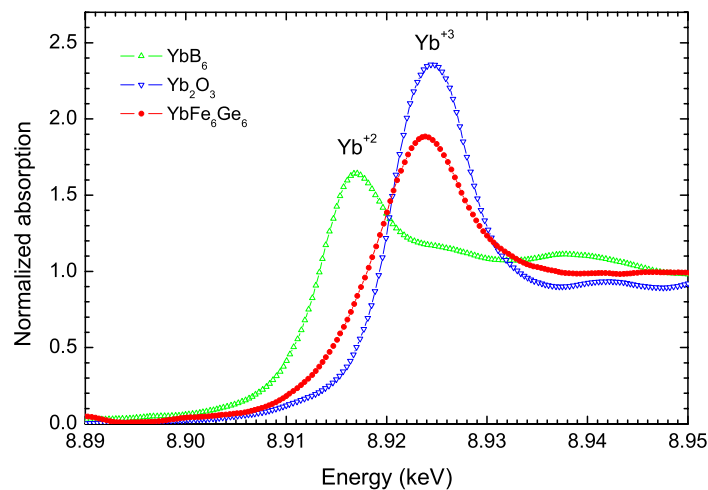
Figure 8. Ytterbium L$_{III}$ x-ray absorption near-edge structure (XANES) of YbFe$_6$Ge$_6$, compared to those of Yb$_2$O$_3$ and YbB$_6$.

To remove this suspicion, we measured the L$_{III}$ XANES spectrum of crushed YbFe$_6$Ge$_6$ crystals, presented in figure 8 together with those of Yb$_2$O$_3$ and YbB$_6$, used as trivalent [21] and divalent [22] references respectively. Despite the reduced peak size of YbFe$_6$Ge$_6$ compared to Yb$_2$O$_3$, which could be attributed to differences in the metallic versus ionic environment, it is clear from the peak position that the Yb ion is essentially trivalent in YbFe$_6$Ge$_6$, so whatever magnetic response it has is indeed being masked by the dominant response of the Fe ions.

4. Discussion

The anisotropic magnetization experiments performed on our single crystals clearly establish the occurrence of a low-temperature anomaly in the magnetic behaviour of YbFe$_6$Ge$_6$, and our collective set of experimental data gives support to the idea that the anomalous behaviour results from a sudden reorientation of the Fe spins, as previously suggested by neutron diffraction and Mössbauer experiments on polycrystals [16]. The destabilization of the simple axial AFM configuration at lower temperatures is almost certainly the precursor phenomenon which allows the otherwise rigidly aligned Fe spins to become more susceptible to other interactions. However, this destabilization occurs in FeGe and in most of its derived RFe$_6$Ge$_6$ compounds, whereas the anomaly has only been documented for R = Yb in this series. So the natural question that follows is: what is unique about YbFe$_6$Ge$_6$ that may be causing this behaviour?

Given that Yb is an ion with unstable 4f shell, it is very tempting to initially suspect that 4f-conduction electron hybridization is somehow related to the unique behaviour, and this was in fact one of our main motivations to pursue this matter, since a compound featuring the coexistence of hybridized 4f states with ordered 3d moments can be potentially very interesting and rich in phenomena to explore. However, our heat capacity measurements showed no significant sign of effective electronic mass enhancement in comparison with LuFe$_6$Ge$_6$, and resistivity shows no sign of enhancements due to Kondo scattering—both of which are natural consequences of hybridized f–d states. This leads us to conclude that, at ambient pressure, the Yb sub-lattice is at best no more than a local-moment paramagnet, at least down to 1.8 K, and the material's magnetic behaviour is dominated by the Fe spins.

A second possible approach to attempt an explanation for the anomaly would be to invoke a structural disorder-induced origin of the effect, given the easiness with which part of the Yb ions may be occupying 1a sites as shown in figure 1. However, once again we are faced with the fact that such disorders are known among all members of the RFe_6Ge_6 series and, if anything, the measured $YbFe_6Ge_6$ sample is less disordered than other crystals we have grown in the family, since it has the highest value of RRR we have obtained so far.

A natural consequence of the disorder-induced scenario is that the effect should be significantly dependent on sample preparation and thermal history. Indeed, we could observe relevant differences in the measured transitions of earlier batches, including intermediate steps along the transition, indicative of intermediate spin configurations (or inhomogeneous samples). In fact, these characteristics (plus the different field behaviour for the two measured orientations) allow our results to be reconciled with the observations of Mazet and Malaman, that the spin reorientation in their polycrystalline sample began at 85 K and only about 20% of the Fe spins deviated from the *c*-axis at 4.2 K. Unfortunately, there were no intentional, systematic parameter modifications between our batches that could allow further insight into the relationship between growth conditions and final magnetic behaviour. Such a systematic study would be an interesting future work, as well as the effects of post-growth annealing on the crystals.

From all the experimental evidence available, it seems that the origin of the drastic spin reorientation effect may actually result from the conjunction of several factors, namely:

(1) the destabilization of the axial Fe spin arrangement upon cooling;
(2) a small but non-negligible Yb-Fe interaction of peculiar RKKY or some other origin;
(3) a crystal field anisotropy of the Yb ions which competes with the Fe easy axis arrangement; and
(4) the presence of disordered sites which may act as catalysts to initiate a cascade effect among Fe spins that are strongly coupled but subject to competing forces.

5. Conclusion

The successful growth of single crystals of $YbFe_6Ge_6$ and $LuFe_6Ge_6$ has allowed us to investigate their magnetic anisotropy in the antiferromagnetically ordered state, and directly observe a sudden change in magnetic behaviour of $YbFe_6Ge_6$ at about 63 K, due to a drastic reorientation of the Fe spins, an unusual effect for the RFe_6Ge_6 series where the Fe and R sub-lattices are known to behave quite independently. Our work has answered some of the questions raised by previous investigations which showed evidence of such an effect to occur in this compound, and eliminated Yb 4f-conduction electron hybridization as a likely candidate to explain its occurrence. However, the actual source of the effect, and especially the nature and strength of the Yb–Fe interaction which is almost certainly the crucial element behind this unique behaviour, remains an open question to be investigated in further detail through more powerful experimental techniques on the now available crystals. The possibility of inducing hybridization in the Yb electronic levels and following the interactions between these and the ordered Fe spins may be a worthwhile endeavour, as well as mapping of how thermal history affects disorder and magnetic behaviour in this compound.

Acknowledgments

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