RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 57, NUMBER 18 1 MAY 1998-II

Reinvestigation of long-range magnetic ordering in icosahedral Tb-Mg-Zn

Z. Islam, I. R. Fisher, J. Zarestky, P. C. Canfield, C. Stassis, and A. I. Goldman
Ames Laboratory, USDOE and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011

(Received 28 January 1998)

We present results of a study of possible magnetic ordering in the icosahedral phase of Tb-Mg-Zn probed by bulk magnetization measurements and neutron diffraction. Measurements on both crushed single grains and cast polycrystalline samples of Tb-Mg-Zn were performed. Magnetization measurements on both samples reveal only a spin-glass-like transition at approximately 5.8 K. Neutron diffraction from the crushed single grains reveals only short-range magnetic ordering at low temperatures, with no evidence of the long-range magnetic ordering reported previously [Charrier, Ouladdiaf, and Schmitt, Phys. Rev. Lett. **78**, 4637 (1997)]. Likewise, the cast polycrystalline samples exhibit primarily diffuse magnetic scattering at low temperature, but at least one relatively sharp diffraction peak was observed. Our results indicate that for single grain samples there is no long-range magnetic ordering and that, at best, the magnetic ordering in these quasicrystalline alloys is not very robust. [S0163-1829(98)51618-9]

The discovery of a stable icosahedral phase alloy in the R_8Mg$_{42}$Zn$_{50}$ family, where R=rare earth,[1,2] has generated recent interest because of the opportunity for new investigations of magnetism involving localized $4f$ moments on a quasiperiodic lattice. A great deal of previous work has been devoted to investigations of magnetism in quasicrystalline alloys including the metastable Al-Mn icosahedral phase,[3] and the stable Al-Pd-Mn (Ref. 4) and Al-Cu-Fe (Ref. 5) icosahedral alloys. These investigations have revealed either spin-glass-like behavior at low temperature, or a diamagnetic response. In all cases, the magnetism in these $3d$ electron systems appears to be weak, making it difficult to discern the effects of aperiodicity upon magnetic interactions between ions. The existence of a stable icosahedral phase containing rare-earth ions with sizable local moments, offers a unique opportunity to study this issue in detail.

The magnetic properties of the R_8Mg$_{42}$Zn$_{50}$ family of icosahedral alloys have been studied by several groups. Measurements by Hattori and co-workers[6] and Charrier and Schmitt[7] on polycrystalline samples of R_8Mg$_{42}$Zn$_{50}$ (R =Gd, Tb, Dy, Ho, and Er) revealed that the dc susceptibilities exhibit a Curie-Weiss law over a wide temperature range with a negative paramagnetic Curie temperature, indicating antiferromagnetic exchange interactions between the R ions. In this case, the effective moments obtained from the data are close to the free ion values, in striking contrast to the results of similar measurements on alloys such as Al-Mn and Al-Pd-Mn where the effective moment was found to be considerably reduced from the free-atom value.[3,4] At lower temperatures, both ac- and dc-susceptibility measurements on R_8Mg$_{42}$Zn$_{50}$ exhibit a classic spin-glass transition with freezing temperatures, T_f, below 10 K. This has been observed for both polycrystalline samples[6,7] and more recently for single grain samples.[9] The presence of spin-glass-like behavior (and absence of magnetic ordering at low temperature) is consistent with strong geometrical frustration of the moments on an aperiodic lattice.[7]

A more recent paper by Charrier and co-workers,[8] however, presented evidence from powder neutron-diffraction measurements that there is a transition to an antiferromagnetic long-range ordered ground state, at least for R=Tb and Ho. The intensity of the sharp peaks in the diffraction pattern, corresponding to the long-range antiferromagnetic ordering, was quite small and was accompanied by significant diffuse magnetic scattering. Most of the sharp magnetic peaks that appeared at low temperature (T_N=20 K for Tb) could be indexed to an icosahedral lattice with a propagation vector of $(\frac{1}{4},0,0,0,0,0)$, quadrupling the six-dimensional-hypercubic lattice along the five-fold directions. Interestingly, for R=Dy and Er the sharp diffraction peaks carried even less weight in comparison to the diffuse background. Further, magnetic susceptibility data from all of these samples failed to display any significant features in the vicinity of T_N, as determined by the neutron measurements, beyond a deviation from its high-temperature Curie-Weiss behavior.

In this paper we present results from bulk magnetization and powder neutron-diffraction measurements of crushed single grains and cast polycrystalline samples of Tb-Mg-Zn. For the crushed single grains, only short-range magnetic ordering was observed at low temperatures by neutron diffraction, with no evidence of the long-range magnetic ordering reported previously. The cast polycrystalline samples, prepared by rapid cooling followed by an extended anneal, exhibit primarily diffuse magnetic scattering at low temperature, but at least one relatively sharp diffraction peak was observed. Interestingly, the temperature dependence of the intensities of both the sharp and diffuse components agree well with the data of Ref. 8. Our results indicate that for single grain samples there is no long-range magnetic ordering and that, at best, the magnetic ordering in these quasicrystalline alloys is not very robust.

Single grain R-Mg-Zn (R=Y, Er, Ho, Dy, and Tb) quasicrystalline samples were prepared following the technique described previously.[10] In brief, a ternary melt was slowly cooled so as to intersect the primary solidification surface of the quasicrystalline phase, as identified for Y-Mg-Zn by Langsdorf and co-workers.[11] Quasicrystals grown by this technique are large (up to 0.5 cm^3), and have a dodecahedral

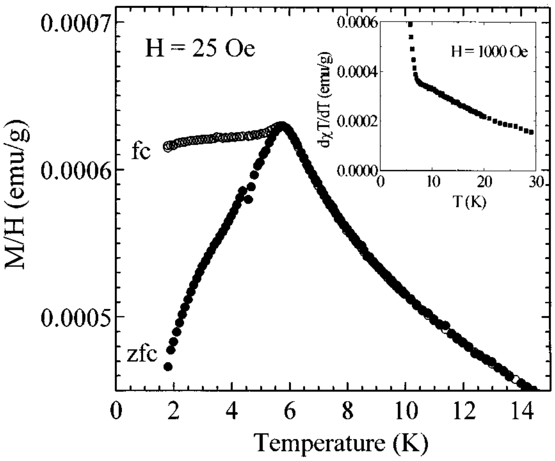

FIG. 1. The low-temperature magnetization of quasicrystalline Tb-Mg-Zn in an applied field of 25 Oe for zero-field-cooled (solid symbols) and field-cooled (open symbols) histories. Inset shows $d(\chi T)/dT$ as a function of temperature in an applied field of 1000 Oe (zero-field-cooled).

growth habit with pentagonal facets. Powder x-ray diffraction of crushed single grains and transmission electron microscopy of individual thin fragments both indicate a high degree of structural order, with little or no phason strain. Electron microprobe analysis indicated a composition for the Tb-containing quasicrystalline phase of $\mathrm{Tb}_{8.7\pm0.2}\mathrm{Mg}_{34.6\pm0.3}\mathrm{Zn}_{56.8\pm0.3}$. Here, we should also point out that at least one crystalline phase (rhombohedral), close in composition to the icosahedral phase of R-Mg-Zn, can also be grown in single-crystal form from the ternary melt.[10] Electron microprobe analysis indicated a composition for the Tb-containing rhombohedral phase of $\mathrm{Tb}_{7.1\pm0.2}\mathrm{Mg}_{31.1\pm0.7}\mathrm{Zn}_{61.6\pm0.7}$. In fact, further investigations have shown that the R-Mg-Zn ternary phase diagram is particularly rich, and several other compounds with compositions neighboring the icosahedral phase are currently under investigation.

A polycrystalline Tb-Mg-Zn sample was also prepared by sealing a nominal composition of $\mathrm{Tb}_8\mathrm{Mg}_{42}\mathrm{Zn}_{50}$ in a Ta tube enclosed in a quartz ampoule, melting the constituents to 800 °C, and then quenching the melt by plunging the crucible into cold running water after removal from the furnace. Particular care was taken to ensure good mixing of the constituents in the melt prior to the rapid cooling. Following the quench, the sample was annealed at 400 °C for 48 h.

The dc magnetization of single grains of the Tb-containing quasicrystalline material was investigated using a quantum design superconducting quantum interference device magnetometer. The magnetization below 20 K in an applied field of 25 Oe was measured for both zero-field-cooled (zfc) and field-cooled (fc) histories, while the high-temperature susceptibility (χ up to 350 K) was measured in a field of 1000 Oe (all data were taken while warming the samples). Detailed results of the magnetic and transport properties of quasicrystalline R-Mg-Zn (R=Y, Er, Ho, Dy, and Tb) will be presented elsewhere.[9]

As shown in Fig. 1, the low-temperature magnetization of a single grain of quasicrystalline Tb-Mg-Zn shows a remarkably clear example of a spin-glass freezing transition. Above the spin-glass freezing temperature ($T_f = 5.8$ K, defined here as the maximum in the zero-field-cooled magnetization), both zfc and fc data are identical. However, below T_f the zfc magnetization is significantly lower than the fc data, which are almost temperature independent. The zfc magnetization below T_f is strongly affected by relaxation processes, empirically governed by a stretched-exponential time relationship.[9] Such relaxation effects make quantitative measurements of $M(T,t)$ for $T<T_f$ very complex. In addition, this relaxation leads to the step seen at 4.2 K in Fig. 1, because the cryostat used for these measurements requires the cycling of temperatures past the boiling point of liquid helium to above T_f followed by a subsequent zfc to just above 4.2 K. The inset to Fig. 1 shows the temperature derivative of the product χT, which is often a sensitive method to expose magnetic transitions. While the spin-glass freezing temperature is evident in this plot, there is no evidence for any other magnetic transitions. More specifically, there is no feature seen at 20 K, the transition temperature reported in Ref. 8. Similarly, no magnetic transitions were observed above the spin-glass freezing temperature for the other rare-earth-containing quasicrystals.[9] Magnetic measurements of the polycrystalline Tb-Mg-Zn sample prepared by rapid cooling were similar to those described above except for an overall reduction in magnitude of the magnetization, and some changes in the shape of the spin-glass cusp. In particular, no distinct feature

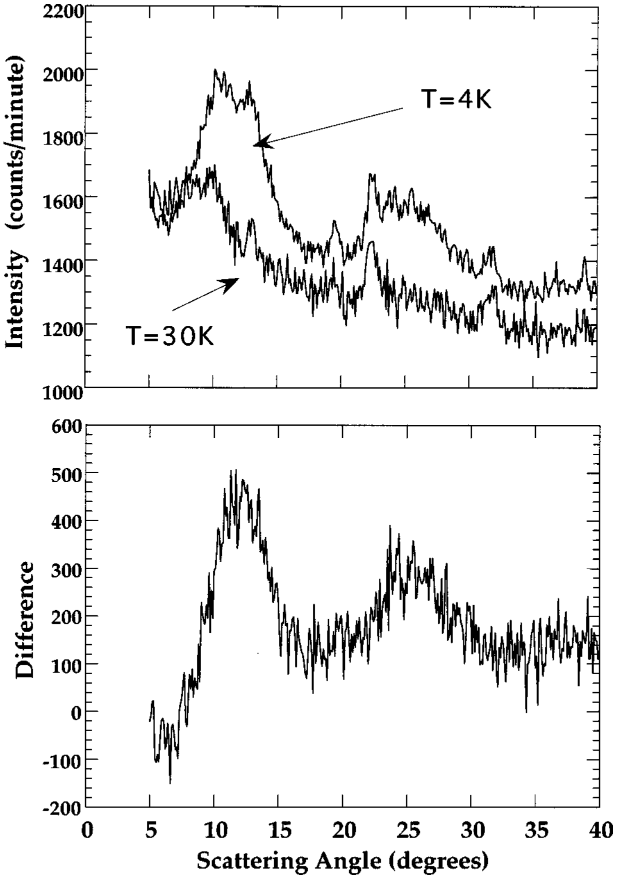

FIG. 2. The top panel displays the neutron-diffraction data taken at 4 and 30 K on the crushed single grains of icosahedral Tb-Mg-Zn. The data in the bottom panel results from a subtraction $[I(4\ \mathrm{K}) - I(30\ \mathrm{K})]$ of the data from the top panel, emphasizing the onset of short-range magnetic ordering, and the absence of any sharp magnetic component, at low temperature.

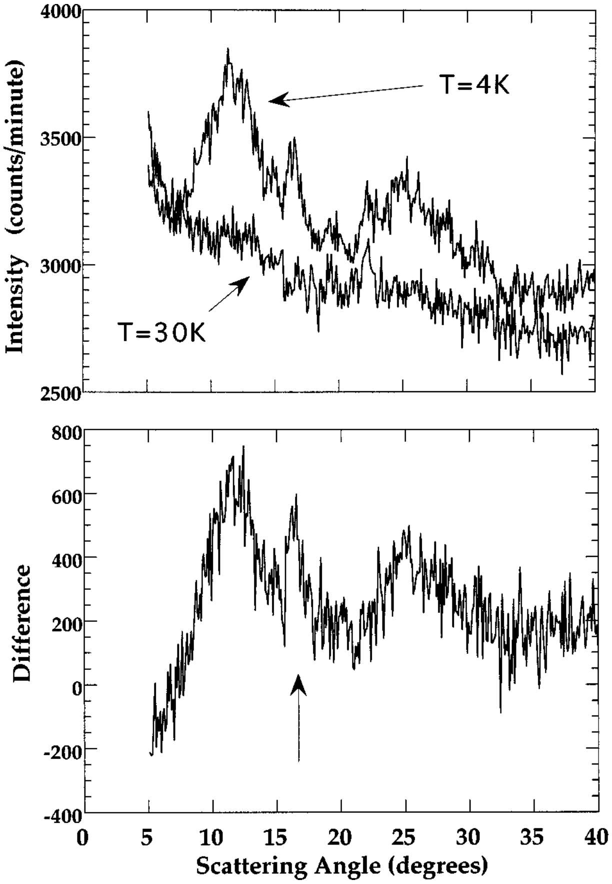

FIG. 3. The top panel displays the neutron-diffraction data taken at 4 and 30 K on the polycrystalline ingot of icosahedral Tb-Mg-Zn. The data in the bottom panel results from a subtraction $[I(4\,\mathrm{K}) - I(30\,\mathrm{K})]$ of the data from the top panel. The appearance of a sharp peak at approximately 16.5° (shown by arrow) in addition to the diffuse magnetic scattering should be noted.

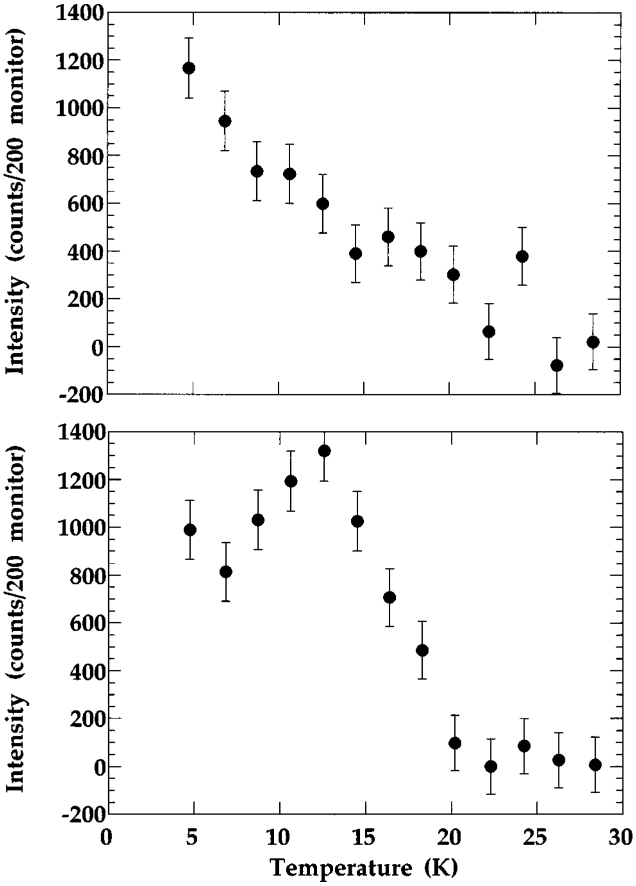

FIG. 4. The temperature dependence of the diffuse (top) and sharp (bottom) components of the pattern shown in Fig. 3 (see text).

in the magnetization at the reported T_N was observed.

In order to study both the possibility of long-range magnetic ordering and the diffuse magnetic scattering observed previously, neutron powder-diffraction studies were performed on both crushed single grains of the icosahedral phase (to reduce or eliminate second phase contamination) and the cast polycrystalline ingots described above. Single grain neutron-diffraction measurements are planned in the near future. Prior to the neutron powder-diffraction measurements, x-ray powder diffraction was used to check the quality of both the crushed single grain sample and the polycrystalline ingot. Within the resolution of these measurements (on the order of 5%), the sample composed of crushed single grains was single phase, while the polycrystalline ingot contained several additional lines. Some of these lines could be indexed to the ternary rhombohedral phase mentioned above, while other contributions could not be identified. The neutron-diffraction measurements were made on the HB1A triple-axis diffractometer at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory. Pyrolytic graphite (002) monochromator and analyzer crystals were used to obtain fixed incident neutron energy of 14.7 meV. A graphite filter was employed to eliminate higher-order harmonics in the beam. The powder samples were mounted on the cold finger of a Heliplex cryogenic refrigerator with a base temperature of approximately 4 K.

The essential results of these measurements are summarized in Figs. 2, 3, and 4. In Fig. 2, we show the data for the crushed single grain sample taken at 30 and 4 K. The bottom panel of Fig. 2 displays the difference $[I(4\,\mathrm{K}) - I(30\,\mathrm{K})]$ in order to emphasize any changes between the patterns taken at these two temperatures. While the difference plot clearly indicates the onset of short-range magnetic order at low temperature, we do not see any evidence of sharp magnetic Bragg peaks, in contrast to the measurements of Charrier *et al.*[8]

In Fig. 3, we plot the data taken at the same two temperatures on the polycrystalline ingot. Again, the difference plot clearly shows the onset of short-range magnetic ordering at low temperature. In addition, one relatively sharp peak [full width at half maximum (FWHM) $\approx 1°$], at approximately 16.5°, appears at low temperature. We were not able to index this peak relative to the nuclear peaks of the icosahedral phase or the rhombohedral phase mentioned above. However, the position of this peak roughly corresponds to one of the two peaks that could not be indexed by Charrier *et al.*, except perhaps as a second harmonic (0.5,1,0,0,0,0) of the magnetic structure. The temperature dependence of both the sharp and broad magnetic components was measured by sitting at the respective maxima of intensity while varying the sample temperature. These data are shown in Fig. 4, after subtracting a background intensity measured at those positions between 25 K and 30 K. Interestingly, the temperature dependence for both the diffuse and sharp components is quite similar to that observed by Charrier *et al.* In particular, both the diffuse and sharp components appear upon cooling below approximately 20 K.

The origin of the discrepancy between the results of this study and the previous work is not clear. One possibility, of course, is that the weak sharp peaks observed in the prior experiments arise from other phases, perhaps crystalline, that may be present in multigrain samples prepared by conventional casting methods. We have found, for example, that the crushed single grains of icosahedral Tb-Mg-Zn are ‘‘clean’’ within experimental detection limits, while the cast ingots, prepared by our group, contain several impurity phases, at least one of which includes the rare earth as a component. It is worth noting here that while susceptibility measurements of the icosahedral phase of Tb-Mg-Zn do not evidence long-range magnetic ordering at low temperature, susceptibility measurements of the rhombohedral phase do show the onset of magnetic order at approximately 14 K.[9] Refinements of both the chemical and magnetic structure of the rhombohedral phase are planned.

Virtually all of the sharp lines shown in Ref. 8, however, could be indexed quite well, by the authors, to a magnetic structure based upon the icosahedral phase structure as discussed above. This leaves us with the interesting possibility that magnetic ordering in the R-Mg-Zn system may be quite sensitively dependent upon composition, the degree of structural order, or other extrinsic effects. For example, it is not yet clear whether the R-Mg-Zn alloys form as line compounds or if the phase diagram has some width to it allowing for small differences in the concentration of, say, the rare-earth component. Dilution studies as well as investigations of the effects of preparation method are currently in progress.

Two conclusions may be drawn from the present study concerning magnetic order in the Tb-Mg-Zn icosahedral phase. First, we have demonstrated that single grain samples of $\mathrm{Tb_{8.7}Mg_{34.6}Zn_{56.8}}$ manifest only short-range magnetic ordering above 4 K. What also seems to be clear from the present study, as well as from the prior investigation[8] (given the differences observed from sample to sample in the rare-earth series) is that the reported quasiantiferromagnetic ordering in R-Mg-Zn is quite fragile. This result itself is intriguing, and could quite conceivably result from the complexity or frustration introduced by a distance-dependent Ruderman-Kittel-Kasuya-Yosida exchange coupling between ions on a quasiperiodic lattice. Further experimental and theoretical work in this area is clearly indicated.

We would like to thank A. F. Panchula for his help in sample preparation. We are also grateful to B. Charrier and D. Schmitt for stimulating discussions. Ames Laboratory is operated for the U.S. Department of Energy under Contract No. W-7405-Eng-82. This work was supported by the Director for Energy Research, Office of Basic Energy Sciences.

---

[1] Z. Luo, S. Zhang, Y. Tang, and D. Zhau, Scr. Metall. Mater. **28**, 1513 (1993).

[2] A. P. Tsai *et al.*, Philos. Mag. Lett. **70**, 169 (1994).

[3] K. Fukamichi *et al.*, J. Phys. F **17**, 743 (1987).

[4] See, for example, S. Matsuo *et al.*, J. Phys. Soc. Jpn. **62**, 4044 (1993).

[5] T. Klein, C. Berger, D. Mayou, and F. Cyrot-Lackmann, Phys. Rev. Lett. **66**, 2907 (1991).

[6] Y. Hattori *et al.*, J. Phys.: Condens. Matter **7**, 2313 (1995).

[7] B. Charrier and D. Schmitt, J. Magn. Magn. Mater. **171**, 106 (1997).

[8] B. Charrier, B. Ouladdiaf, and D. Schmitt, Phys. Rev. Lett. **78**, 4637 (1997).

[9] I. R. Fisher, K. O. Cheon, K. Dennis, and P. C. Canfield (unpublished data).

[10] I. R. Fisher, Z. Islam, A. F. Panchula, K. O. Cheon, M. J. Kramer, P. C. Canfield, and A. I. Goldman, Philos. Mag. B **77**, 1601 (1998).

[11] A. Langsdorf, F. Ritter, and W. Assmus, Philos. Mag. Lett. **75**, 381 (1997).