$HoFe_4Al_8$: An unusual spin glass

J. Gal
Department of Nuclear Engineering, Ben-Gurion University of the Negev, 84105 Beer-Sheva, Israel and Nuclear Research Center–Negev (NRCN), P.O. Box 9001, 84190 Beer-Sheva, Israel and Physik-Department (E15), Technische Universität München, D-8046 Garching bei München, Federal Republic of Germany

I. Yaar, E. Arbaboff, and H. Etedgi
Department of Nuclear Engineering, Ben-Gurion University of the Negev, 84105 Beer-Sheva, Israel and Nuclear Research Center–Negev (NRCN), P.O. Box 9001, 84190 Beer-Sheva, Israel

F. J. Litterst, K. Aggarwal, J. A. Pereda, and G. M. Kalvius
Physik-Department (E15), Technische Universität München, D-8046 Garching bei München, Federal Republic of Germany

G. Will and W. Schäfer
Mineralogisches Institut der Universität Bonn, D-5300 Bonn 1, Federal Republic of Germany and Kernforschungsanlage Jülich, D-5170 Jülich, Federal Republic of Germany
(Received 9 March 1989)

We report on the spin-glass behavior of $HoFe_4Al_8$. Irreversible and time-dependent effects in the intensities of magnetic Bragg scattering derived from neutron diffraction reveal this behavior pronouncedly below $T_{SG}=180$ K. Further evidence comes from the dc isothermal and thermoremanent magnetization. The Mössbauer ^{57}Fe spectra show a sudden onset of magnetic hyperfine splitting below T_{SG} and a flat temperature dependence together with irreversible effects under applied magnetic fields. A transition temperature from aligned to random spin-glass states T_{OG} is reported. $T_{OG}=40$–70 K, depending on the applied magnetic field. Most unusual is the lack (or extremely broad) of a cusp in the ac susceptibility in the vicinity of T_{SG}.

The relevance of the spin-glass (SG) concept and especially of spin-glass models with respect to real systems remains controversial. It is still questionable whether there exists a phase transition to a random state of long-range character, or whether the experimental evidence demonstrates some type of a transition due to nonequilibrium effects.[1] Such effects may be found in experiments with finite time windows by observing phenomena with anomalously long relaxation times.

Traditionally a SG state is claimed when there exists an irreversible term in the magnetization below the SG transition temperature T_{SG} together with a cusp in the ac susceptibility at T_{SG}.[2,3] Theoretical treatment of spin glasses and frustrated magnetic systems simulate some characteristic properties of the spin-glass state, though the interpretation of the ac susceptibility cusp has been criticized by several authors. Their Monte Carlo calculations predict a round maximum and no cusp at the SG transition temperature T_{SG}.[1,4]

In this paper we report on $HoFe_4Al_8$, which exhibits most of the properties of a spin glass, but the ac susceptibility shows a nearly flat behavior with no cusp around the expected T_{SG}. Snapshots of this glassy system at different time windows with and without applied magnetic fields are reported and discussed.

$HoFe_4Al_8$ was prepared by arc melting in a dry argon atmosphere the nominal amounts of the constituents, followed by annealing at 800 °C for 1 week. X rays and neutron patterns confirmed the crystallization of a body-centered tetragonal (space group $I4/mmm$) structure.[5] The neutron-diffraction measurements were performed on the powder diffractometer of Bonn University in the Kernforschungsanlage Jülich. This diffractometer is equipped with the linear position-sensitive detector JULIOS.[6] The wavelength used was 1.09 Å. Magnetic fields up to 6 T, perpendicular to the neutron beam, were applied by a split superconducting coil. The ac susceptibility measurements were performed with two different instruments; a triple-coil ac susceptometer (20 Hz–20 kHz) described elsewhere[7] and a high-sensitivity (better than 10^{-6} emu/g) ac susceptometer. The dc magnetization measurements were taken with a vibrating-sample magnetometer (VSM) in a He-flow cryostat. The ^{57}Fe Mössbauer transmission experiments were performed in a conventional, variable-temperature cryostat.

The neutron-diffraction patterns below ≈ 180 K reveal the appearance of satellites to the (200) and (220) nuclear reflections, depending on the cooling procedure of the sample. Changes in the intensities of the $(200)\pm$ and $(220)\pm$ satellites together with time-dependent effects are clearly recognized below 150 K down to ≈ 20 K. Below 20 K the system seems to be stable and no temperature-dependent effects are observed. The appearance of these satellites at temperatures below 20 K has been interpreted as antiferromagnetic order with a conical spiral component of the Fe sublattice.[8] The presence of the (110) reflection in the neutron diffractogram is a sensitive indicator for a ferromagnetic ordering of the Ho sublattice.[9] However, in most of the cooling cycles no indication of the (110) reflection down to 4 K has been recorded in the neutron data. During a few of these cooling cycles the (110) reflection appeared at 16 K. Its intensity corresponded to $\approx (0.6\text{–}2)\mu_B$ per Ho ion. This small value of the moment together with the anomalies in the temperature behavior of the (200)±, (220)±, and (110) reflections gave us the first hint that the Ho and the Fe spin directions could, in fact, be randomly frozen in the lattice within spin-glass configurational states. Further support came from the Mössbauer observations of local spin ordering. In order to check this assumption the sample was cooled from room temperature to 4 K where an external magnetic field was switched on; in this procedure the Ho moments aligned and froze parallel to the direction of the field. The Ho spin alignment is sensed by the intense appearance of the (110) reflection associated with the disappearance of the (200)±, (220)± satellites (Fig. 1). From the (110) intensity we derived the dependence of the ordered moment on the applied magnetic field. We get a saturation value of $\mu_{\mathrm{ORD}} \approx 8\mu_B$ (Fig. 2). When switching off the external field B_{APL}, the Ho moments remain frozen ferromagnetically. A decrease of ≈5% per hour of the (110) reflection intensity together with gradual reappearance of the (200)±, (220)± satellites (Fig. 1), indicates the existence of isothermal remanent ordered moments at the Ho and the Fe sublattices.

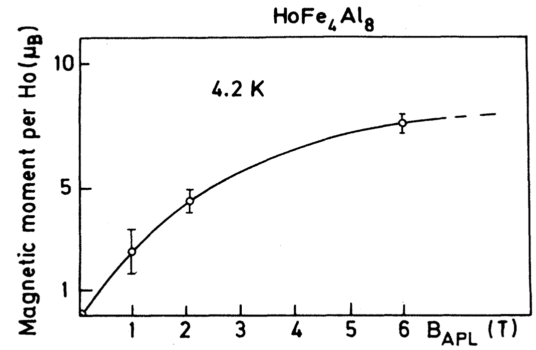

FIG. 2. Ordered frozen moment as a function of applied magnetic field derived from the (110) reflection.

We were able to determine the ordering temperature (T_{OG}) of the frozen Ho sublattice by observing the temperature dependence of the (110) reflection within 1 h after switching off the external field. T_{OG} represents the transition temperature between the aligned SG state to a random SG state. This ordering temperature is dependent on B_{APL} and varies from 40 (at 2 T) to 70 K (at 6 T).

The isothermal remanent and thermoremanent dc magnetization differ markedly and are strongly dependent on the applied magnetic field in which the magnetization measurement is being performed. Typical thermoremanent magnetization measurements which were performed at an applied field of 0.03 T are given in Fig. 3. The spin-glass transition temperature T_{SG} is defined as the point where the irreversible component of the magnetization becomes zero. The spin-glass temperature T_{SG} derived from our dc magnetization measurements depends on the applied field and cooling speed. It varies from 140 to 180 K. Another way to determine T_{SG} is to search for a deviation from Curie-Weiss behavior at high tempera-

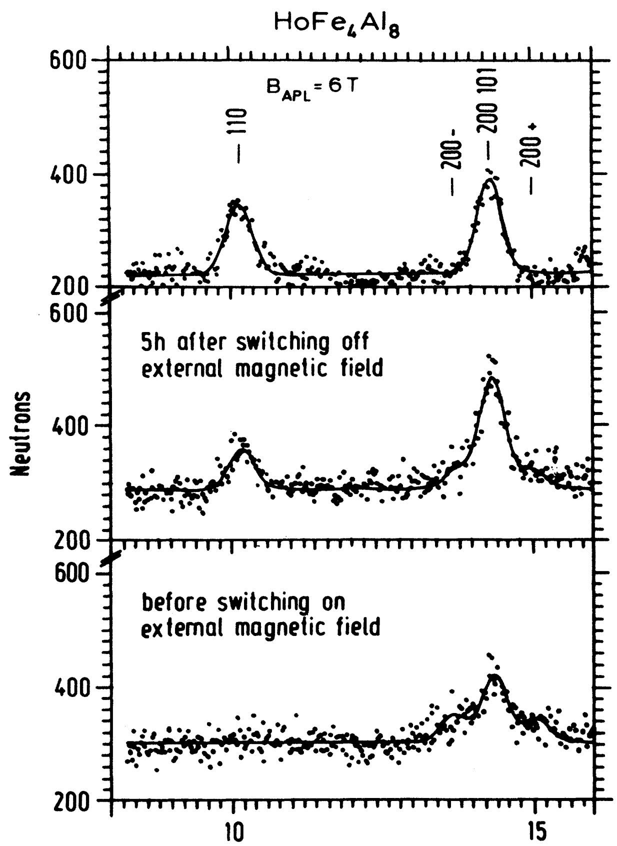

FIG. 1. Low angle neutron-diffraction pattern of $HoFe_4Al_8$ at 4.2 K. (a) Under applied external magnetic field B_{APL}. (b) 5 h after switching off B_{APL} of 6 T. (c) Slow cooling at zero field of the sample.

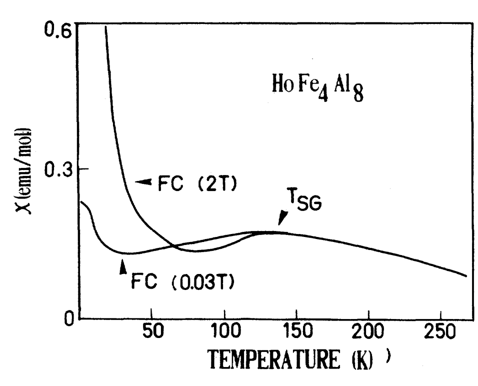

FIG. 3. dc magnetization curves of $HoFe_4Al_8$ cooled under applied magnetic field (FC) of 2 and 0.03 T. The measurements were performed at an applied field of 0.03 T. The sharp transition at $T_{\mathrm{OG}} \approx 50$ K indicates Ho spin alignment due to the applied external magnetic field (see text).

tures. This is observed in the reciprocal susceptibility curves already below 190 K. The curves flatten at ≈ 160 K until 50 ± 10 K where a sharp decrease (or increase in the magnetization, as shown in Fig. 3) indicates ferromagnetic ordering. This confirms the value of T_{OG} derived by the neutron measurements.

The ^{57}Fe Mössbauer spectra show nonmagnetic quadrupole split spectra from room temperature down to 175 ± 5 K indicating a paramagnetic regime. Below this temperature a superposition of a magnetically split pattern and a paramagnetic doublet is clearly recognized (Fig. 4). By application of external magnetic field (6 T) the spectra show temperature-dependent irreversibilities in the I_2 and I_5 ($\delta m_z = 0$ nuclear transitions) absorption lines.[10] The spectra were fitted by assuming a superposition of a quadrupole doublet and a magnetically split pattern with distribution of hyperfine fields. Their relative occupation depends on the temperature. The derived average of hyperfine fields at zero-field cooling shows a moderate decrease as a function of the temperature with a sharp cutoff at 180 ± 5 K (Fig. 5). As the ac susceptibility (see below) and the neutron-diffraction measurements indicate no magnetic transition at 180 K we relate this sharp transition to the establishment of frozen local spin directions, namely to a spin-glass state at the Fe site. Below 20 K the Mössbauer ^{57}Fe hyperfine field is constant and could be interpreted as due to magnetic order in accord with the neutron-diffraction results.

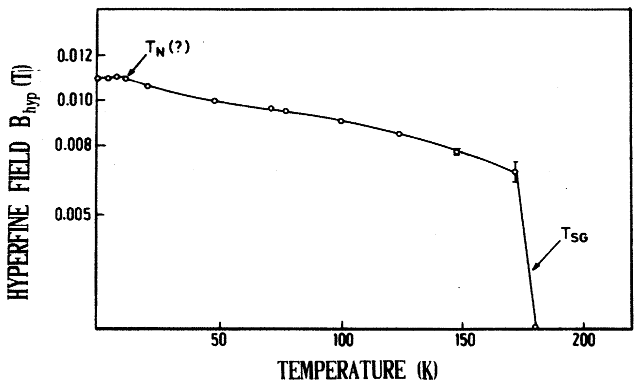

FIG. 5. ^{57}Fe average hyperfine field B_{hyp} as a function of temperature. Note the sharp cutoff at 170 K.

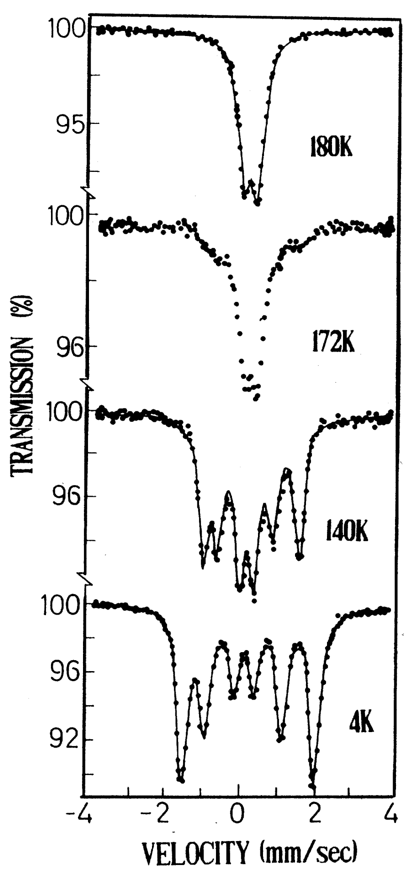

FIG. 4. Typical ^{57}Fe Mössbauer spectra of $HoFe_4Al_8$. The hyperfine Zeeman splitting below 180 K indicates local spin direction and is related to a spin-glass transition. The solid line represents a theoretical model described in the text.

The ac susceptibility was measured from 300 to 30 K by the two different ac susceptometers described above. At frequencies from 20 Hz to 20 kHz, both reveal a low signal with no sign of a cusp close to the expected T_{SG}.

In summary, the intermetallic $HoFe_4Al_8$ exhibits the following experimental properties: (a) onset of magnetic hyperfine splitting at the ^{57}Fe nucleus below $T_{SG} = 180$ K indicating a frozen local spin direction; (b) irreversible magnetic Bragg scattering observed by neutron diffraction (remanent ordered moments which decay slowly with time); (c) irreversible components in the isothermal and thermoremanent dc magnetization below T_{SG}; and (d) high sensitivity to cooling and annealing procedures (history effects).

These properties are usually related by the experimentalists to the establishment of a spin-glass state in a magnetic system.[2] An essential proof for establishment of a SG state are the Mössbauer spectra which should indicate a local spin-directional ordering below T_{SG}.[10] Irreversibilities and time-dependent effects in the Mössbauer pattern under applied magnetic fields are also an indicator. Irreversibilities in the neutron Bragg scattering with strong history effects below T_{SG} are expected by any realistic Heisenberg-type SG model.[11,12] The possibility to align the spins parallel to the direction of an applied magnetic field for a long period is characteristic of any SG system. But the confirmation of this situation is limited to a concentrated (periodic lattice) one. The slow transition from an aligned to a random state and the existence of $T_{OG} < T_{SG}$, could be explained by some of the SG models; the order parameter in a SG is expected to decay with time,[1] especially under forced aligned conditions. Time-dependent effects and relaxation effects are predicted by the dense configurational ground states[1,11] and by the SG clustering models.[13,14] Nonlinear terms in the magnetization below T_{SG} are predicted by the mean-field theory for the SG state.[2,3]

In conclusion, each of the experimentally observed phenomena could be explained by some of the available SG models. The absence of a cusp in the ac susceptibility, in the vicinity of T_{SG}, introduce a difficulty in defining the system as an archetypal spin glass. Although some theoretical models do predict a broad maximum instead of a sharp cusp,[1,4] we observe a nearly flat behavior. Still, an extremely broad maximum should not be excluded but must be confirmed with a better resolution instrument. As the precise nature of the magnetic order associated with the cusp in the ac susceptibility is controversial,[1,3] our present experimental results show that a SG system may also exist without a significant cusp. Preliminary measurements on other compounds of the RFe$_4$Al$_8$ family (R=Tb,Er,Dy) indicate very similar SG behavior. All this leads to the conclusion that we probably face a new type (or a second class) of spin-glass system.

At low temperatures the R moments in the RFe$_4$Al$_8$ systems tend to order ferromagnetically while the Fe moments order antiferromagnetically.[8] Frustration may be caused by the Ruderman-Kittel-Kasuya-Yosida exchange coupling of the Ho and Fe moments mediated by the randomly distributed Fe ($\approx 5\%-8\%$) and Al vacancies in the Al positions.[15,16] One probably deals with a so-called concentrated highly frustrated spin system which is characterized by a lack (or extremely broadened) of a cusp in the ac susceptibility and a sharp Mössbauer hyperfine transition at T_{SG}. In addition, the moderate linear change (non-Brillouin) of the hyperfine fields and the neutron Bragg intensities as a function of the temperature that smoothly reaches an ordered state, could argue for hierarchical ordering within the spin-glass state.[17]

This work has been funded by the German Federal Minister for Research and Technology [Bundesminister für Forschung and Technologie (BMFT)] under Contracts No. 03-GALBEE, No. 03-KALTUM, and No. 03-WIBON and by the National Council for Research and Development, Israel.

[1]D. Staufer and K. Binder, Z. Phys. B **30**, 313 (1978).

[2]D. Chowdhury, *Spin Glass and Other Frustrated Systems* (World Scientific, Singapore, 1986), pp. 1 and 31.

[3]I. Yeung, W. Ruan, and R. M. Roshko, J. Magn. Magn. Mater. **74**, 59 (1988).

[4]D. C. Rapaport, J. Phys. C **10**, L543 (1978).

[5]I. Felner and I. Nowik, J. Phys. Chem. Solids **39**, 951 (1978).

[6]W. Schäfer, E. Jansen, F. Elf, and G. Will, J. Appl. Crystallogr. **17**, 159 (1984).

[7]S. Tapuchi, Ph.D thesis, Ben Gurion University, 1988 (unpublished).

[8]W. Schäfer and G. Will, J. Less-Common. Met. **94**, 205 (1983).

[9]W. Schäfer, M. Grönefeld, G. Will, and J. Gal, in *Proceedings of the Neutron Scattering Symposium, Sydney, Australia, 1987* [Materials Science Forum **27-28**, 243 (1988)].

[10]S. M. Dubiel, K. H. Fischer, Ch. Sauer, and W. Zinn, Phys. Rev. B **36**, 360 (1987).

[11]L. R. Walker and R. E. Walsted, Phys. Rev. Lett. **38**, 514 (1977).

[12]H. Yoshida, S. Mitsuda, H. Aruga, and A. Ito, Phys. Rev. Lett. **59**, 2364 (1987).

[13]J. L. Tholence and R. Tournnier, J. Phys. (Paris), Colloq. **35**, C4-229 (1974).

[14]P. Wohlfarth, Physica B **86-88**, 873 (1977).

[15]J. Gal, H. Pinto, S. Fredo, H. Shaked, W. Schafer, G. Will, F. J. Litterst, W. Potzel, L. Asch, and G. M. Kalvius, Hyper. Interact. **33**, 173 (1987).

[16]W. Schäfer, G. Will, G. M. Kalvius, and J. Gal, in *Proceedings of the International Conference on Neutron Scattering, Grenoble, 1988* [Physica B **156-157**, 751 (1989)]. The analysis of our neutron and Mössbauer data confirm $\approx 6 \pm 2\%$ Fe atoms in the Al $8j$ positions.

[17]S. R. McKay, A. N. Berker, and S. Kirkpatrick, J. Appl. Phys. **53**, 7974 (1982).