

Study of the negative magnetization effect in $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$

A. Bhattacharjee* and R. Feyerherm

*Department of Physics, St. Joseph's College, North Point, Darjeeling 734 104, India
Abteilung NE, Hahn-Meitner-Institut, 14109 Berlin, Germany

Temperature and magnetic-field-dependent magnetization studies of ferrimagnetic $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$ are presented in this paper, which demonstrate that the negative magnetization after field-cooling reported previously is observed only in magnetic fields smaller than 5 kOe. In higher fields probably Zeeman energy dominates the ordering energy and destroys the observed negative magnetization. The absolute value of the ferrimagnetic saturation magnetization = $0.07 \mu_B$, which was estimated from the field dependence of the field-cooled magnetization at 5 K. The memory of the field-cooling procedure could not be destroyed by a magnetic field of 55 kOe.

'MOLECULAR-BASED MAGNET' is a topic of considerable interest in contemporary research in the fields of physics as well as chemistry^{1,2}. These magnets exhibit spontaneous or sublattice magnetizations below critical temperatures. Three strategies have been reported to realize molecular-based magnets using: charge-transfer complexes, organic free radicals, and mixed-metal complexes. Recently, long-range magnetic ordering has been reported in the infinitely extended oxalate-bridged mixed-metal networks of general stoichiometry $A[\text{M}^{\text{II}}\text{M}^{\text{III}}(\text{ox})_3]$, where A = monocation, M = transition metal, ox = oxalate ligand^{3,4}. The great variability of the monocation A and of the $\text{M}^{\text{II}}\text{-M}^{\text{III}}$ metal combination has led to the synthesis of a broad array of compounds exhibiting different magnetic as well as optical phenomena including antiferromagnetic ordering ($\text{M}^{\text{II}} = \text{Mn}$, $\text{M}^{\text{III}} = \text{Fe}$) (ref. 5), spin-glass type behaviour ($\text{M}^{\text{II}} = \text{Fe}$, $\text{M}^{\text{III}} = \text{Fe}_{1-x}\text{Cr}_x$) (ref. 6), short-range magnetic correlations ($\text{M}^{\text{II}} = \text{Cr}$, $\text{M}^{\text{III}} = \text{Cr}$) (ref. 7), and nonlinear optical effect⁸. The crystal structure determinations of several of these compounds have revealed that they generally crystallize in quasi-two-dimensional honeycomb metal-oxalate networks, which are alternately separated by layers of the cation A (refs 9–12). In this report, discussions will be centred on the ferrimagnetic compound $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$.

The magnetic properties of molecular-based ferrimagnetic material $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$, where NBu_4^+ = tetra-*n*-butyl ammonium ion, ox^{2-} = oxalate ion, were first reported by Okawa *et al.*⁴. This compound is found to be ferrimagnetic ($T_N = 43$ K), and a spin-glass-like disordered state was anticipated at temperatures below 40 K. This compound was prepared in a way that the intermetal

linkage $\text{Fe}^{\text{II}}\text{-ox-Fe}^{\text{III}}$ extends three-dimensionally into the entire crystal lattice, since the molecular model consideration indicates that the reactions of η^3 -complex $[\text{Fe}^{\text{III}}(\text{ox})_3]^{3-}$, Fe^{II} ion, and NBu_4^+ ion in 1:1:1 stoichiometry produce an isotropic three-dimensional structure. If the magnetic interaction between the neighbouring metal ions is antiferromagnetic, it is anticipated that the magnetic vectors are assembled by the difference between the spin vectors to afford a ferrimagnet. Mathoniere *et al.*¹³ reported the unit cell parameters of this compound ($a = b = 9.402 \text{ \AA}$, $c = 53.88 \text{ \AA}$) from the powder diffraction profiles indexed on hexagonal system. A large negative magnetization was observed in this compound under 100 Oe and at a temperature below and around 30 K (ref. 13). Later a large number of compounds, general formula $A[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$ wherein A represents different organic cations, were reported by Mathoniere *et al.* to exhibit negative magnetization phenomenon¹⁴. As an explanation of the negative magnetization phenomenon after field-cooling under low magnetic fields according to a theory proposed by Néel¹⁵, a different temperature dependence of the two sublattice magnetizations of Fe^{II} and Fe^{III} has been suggested resulting in a crossover around 30 K (ref. 14). This negative magnetization phenomenon, as observed in $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$ compound under low magnetic field has led us to the systematic reinvestigation into the magnetic properties of this compound in order to obtain a quantitative picture of this phenomenon. Some of the observations obtained in the magnetization measurements for $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$ have been discussed in this paper.

The compound $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$ was prepared in one-pot reaction according to the procedure reported earlier⁴. The required amount of tetra-*n*-butylammonium bromide was added to the aqueous solution of $\text{K}_3[\text{Fe}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$. To the resulting solution another aqueous solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added, which caused immediate precipitation of microcrystals of $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$. The microcrystals obtained by filtration were washed with water and then dried over P_2O_5 in vacuum for one week before use. The compound was obtained as a deep-green microcrystalline powder. The microanalysis data for carbon, hydrogen and nitrogen obtained are in general agreement with the calculated data⁶. The metal compositions in this compound were determined by atomic absorption analysis.

A Quantum Design's MPMS SQUID magnetometer was used for the magnetization measurements and hysteresis curve between ± 55 kOe. The polycrystalline sample (ca. 6 mg) of the compound was placed in an uncoloured gel capsule of RP Scherer GmbH, Germany, (product no. 42016). Temperature dependence between 5 and 300 K of the magnetization were measured under different applied magnetic fields. The field-cooling (FC) measurements were performed after heating the sample

to 100 K and cooling it to liquid He temperature under the applied magnetic fields. Hysteresis curves were measured after zero field-cooling (ZFC) ($H \leq 2$ Oe) and after FC in 1 kOe in the sequence 1 kOe \rightarrow 55 kOe \rightarrow -55 kOe \rightarrow 55 kOe.

Figure 1 shows the temperature dependence of the molar magnetization in a magnetic field of 1 kOe after ZFC and FC. Below the ferrimagnetic transition at 43 K the ZFC data shows the usual behaviour for a compound forming magnetic domains, which cannot move freely at low temperatures. The FC data in contrast behaves highly anomalously. On decreasing the temperature, the spontaneous magnetization rises rapidly to a maximum at about 40 K and then decreases down to a zero net magnetization at a compensation temperature of 27 K. Below 27 K, magnetization decreases monotonously down to 5 K. The net magnetization below 27 K is negative, i.e. net magnetic moment is opposite to the applied magnetic field direction. This measurement was repeated for several applied magnetic fields. Figure 2 shows the temperature dependence of magnetization in the FC mode under different applied magnetic fields. This figure demonstrates the increase of the absolute value of the negative magnetization at 5 K up to a field of about 1 kOe. At higher applied fields, the absolute value of the negative magnetization decreases again. In fields of 5 kOe and larger, the magnetization is positive in the whole temperature range. At very low fields, the zero magnetization occurs at 30 K. This value is consistent with the previously reported value¹⁴. This type of temperature dependence of magnetization for the present compound indicates that the compensation temperature is strongly magnetic field dependent. Such a dependence of the compensation temperature with applied

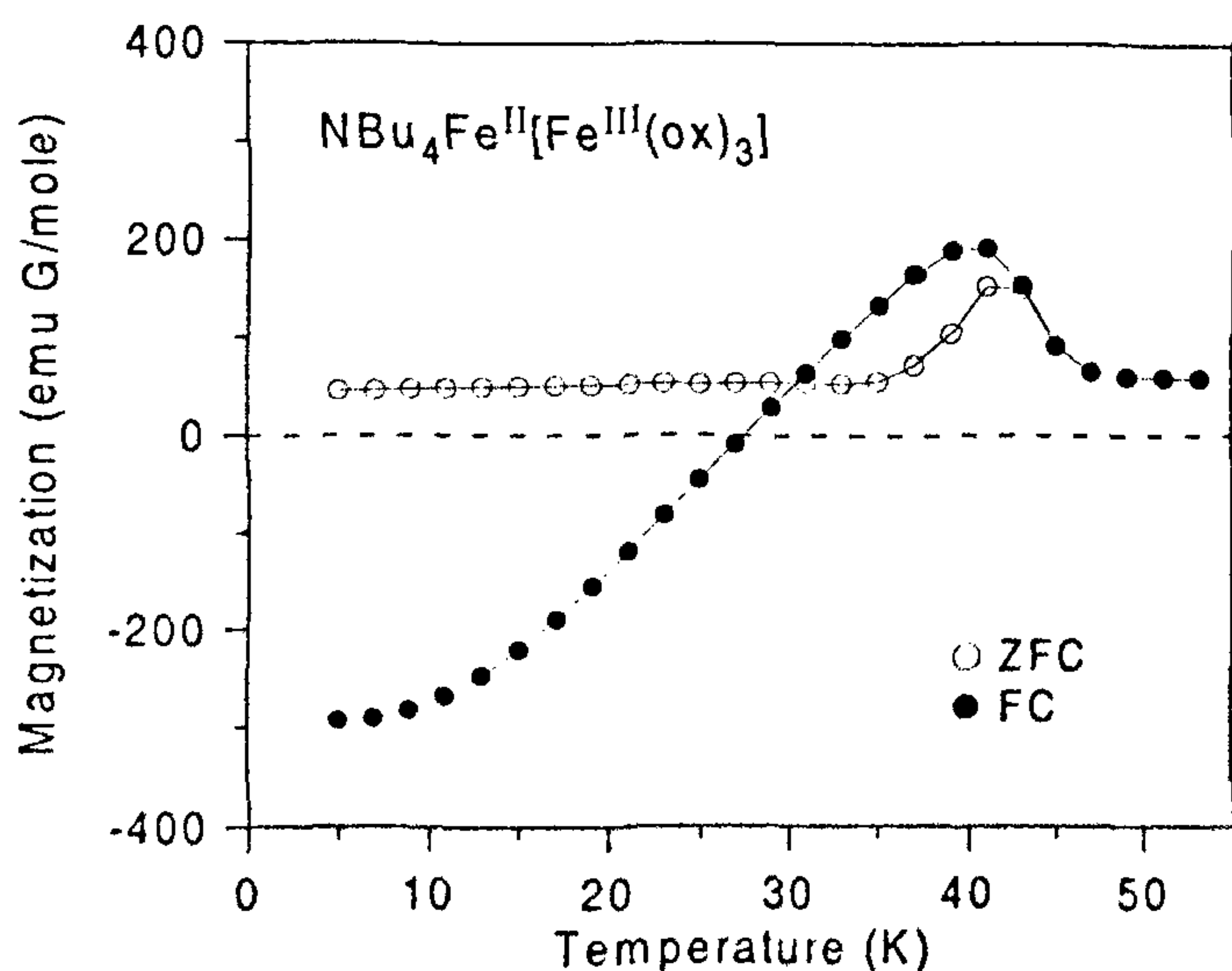


Figure 1. Plot of molar magnetization vs temperature for $\text{NBu}_4\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{ox})_3]$ in zero field-cooled (ZFC) and field-cooled (FC) modes under 1 kOe magnetic field.

magnetic field obtained from the magnetization vs temperature plots under different magnetic fields in FC mode for the present compound is shown in Figure 3.

According to the theory presented in ref. 14, the observed unusual behaviour of the FC magnetization is explained as follows. The sublattice magnetizations of Fe^{II} and Fe^{III} appear to have different temperature dependences such that the sublattice magnetization of Fe^{II} increases more steeply on cooling below the ferrimagnetic transition temperature than that of Fe^{III} . At low temperatures however, the Fe^{III} are expected to reach the larger sublattice magnetization. Therefore, a crossover occurs at a certain temperature, at which the two antiparallel sublattice magnetizations of Fe^{II} and Fe^{III} cancel

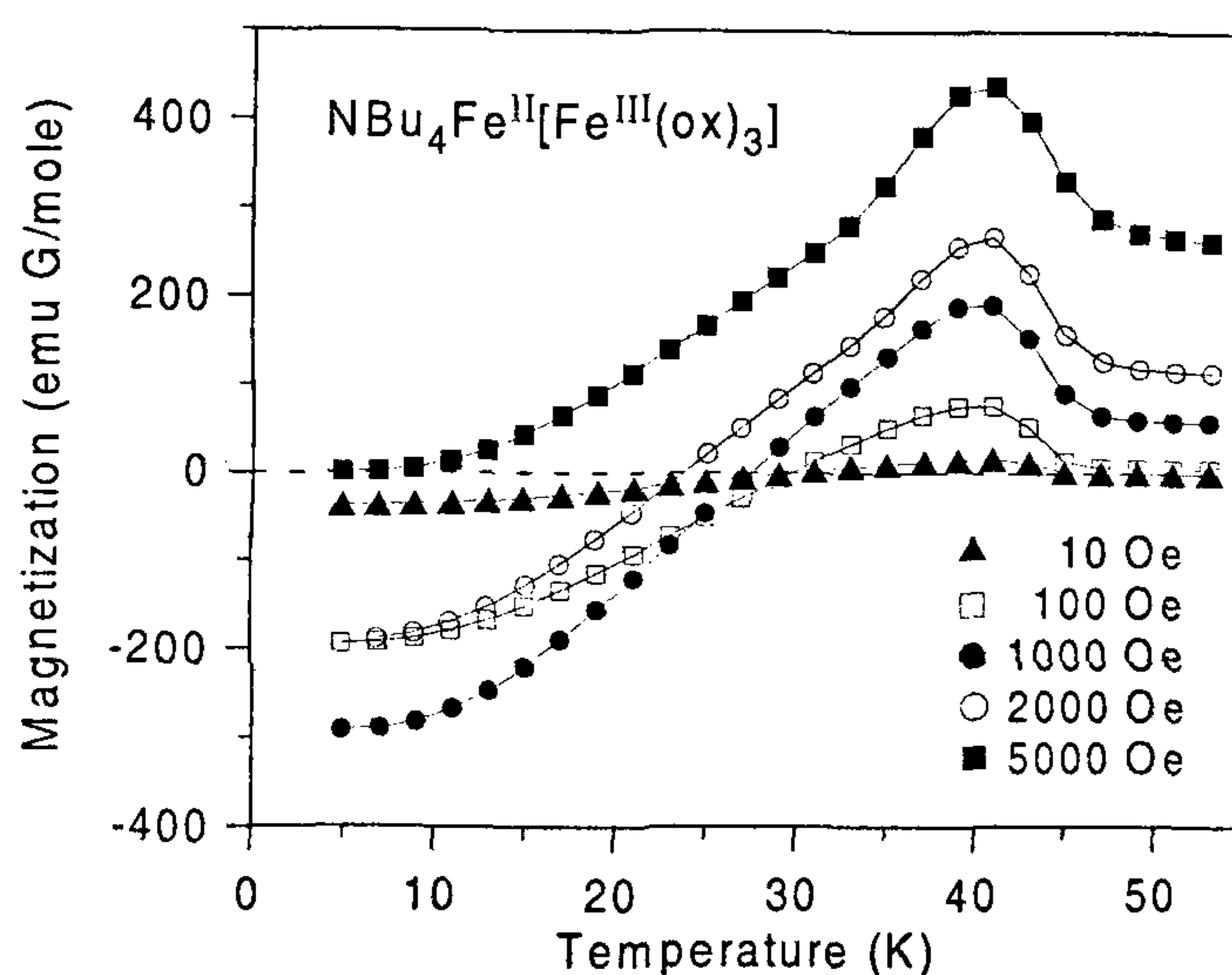


Figure 2. Plot of molar magnetization vs temperature for $\text{NBu}_4\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{ox})_3]$ in FC mode under different magnetic fields.

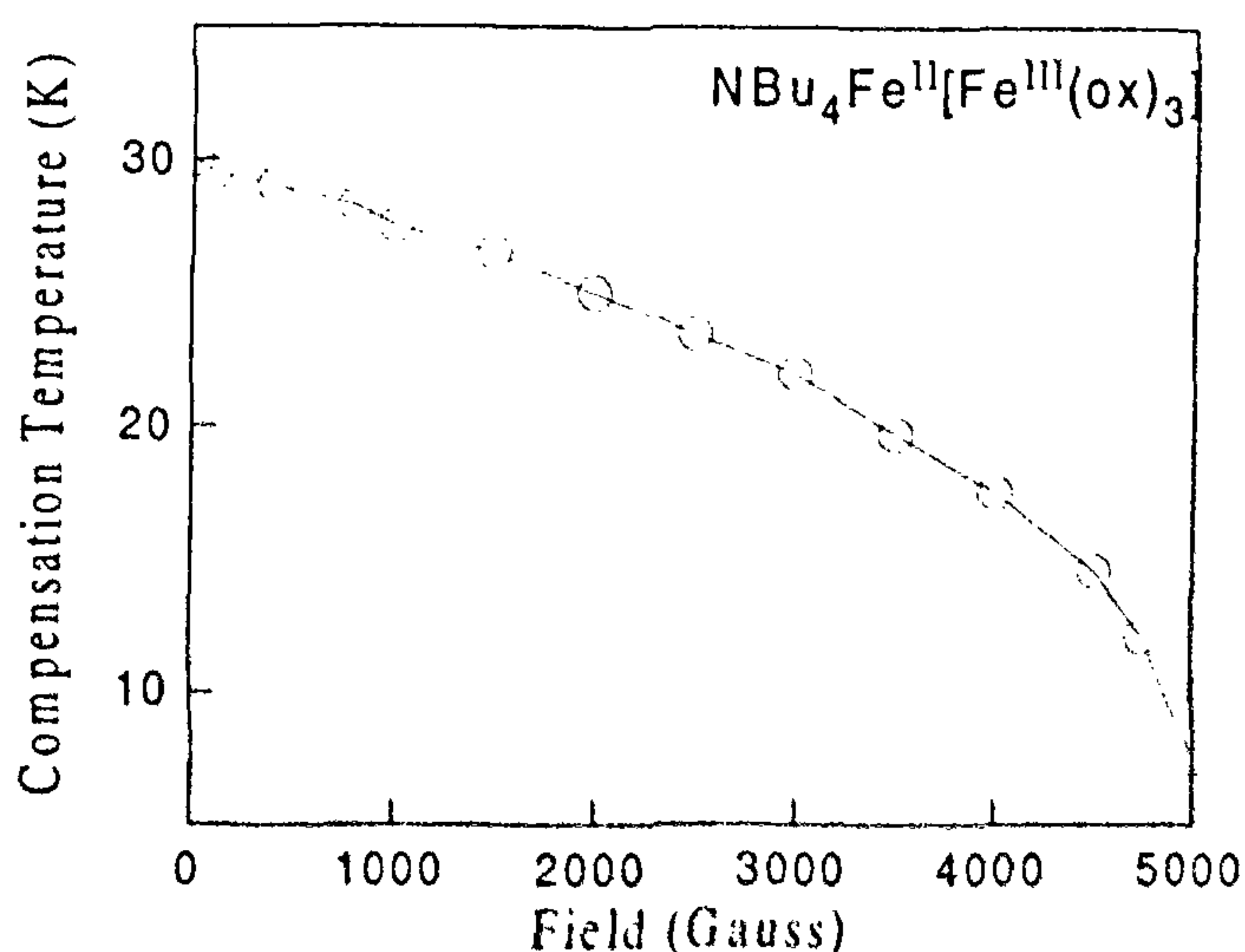


Figure 3. Plot of compensation temperature vs magnetic field for $\text{NBu}_4\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{ox})_3]$.

each other out, resulting in a zero net magnetization. Strictly speaking, the compensation temperature is the temperature at which the spontaneous sublattice magnetizations cancel, i.e. the net magnetization is zero under an applied magnetic field. The magnetic compensation has been reported to occur in some ferrimagnetic compounds such as spinel Co_2VO_4 and garnet $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ (refs 16, 17), LaVO_3 (refs 18, 19), $\text{LaVO}_{3-\delta}$ (ref. 20), and $(\text{Ni}_x\text{Mn}_{1-x})_{13}[\text{Cr}^{\text{III}}(\text{CN})_6]$ (ref. 21). No such effects have been found in the ZFC mode, since in a polycrystalline sample the domains within a ferrimagnetic component will be randomly oriented on cooling in the absence of a magnetic field. Figure 2 reveals that the anomalous magnetic state in the $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$ compound at low temperatures is gradually destroyed with the increasing applied magnetic field. This is perhaps because the Zeeman energy competes more effectively with the ordering energy in higher fields, and at some point rotates the spins that result in a negative sublattice magnetization, in the direction of the applied magnetic field²⁰.

Figure 4 shows the field dependence of the FC magnetization at 5 K. The largest negative magnetization is reached in fields slightly below 1 kOe. Above 2 kOe the field dependence of the magnetization is approximately linear, crossing zero at about 5 kOe. From this field dependence it may be said that the total magnetization has two contributions. First, the contribution resulting from the alignment of the ferrimagnetic domains, and second, a contribution that is linear with the field. The alignment of the ferrimagnetic domains appears to be complete at a field of about 2 kOe, and in higher fields this contribution is constant. The extrapolation of the linear behaviour down to zero field gives a value for this contribution to the magnetization

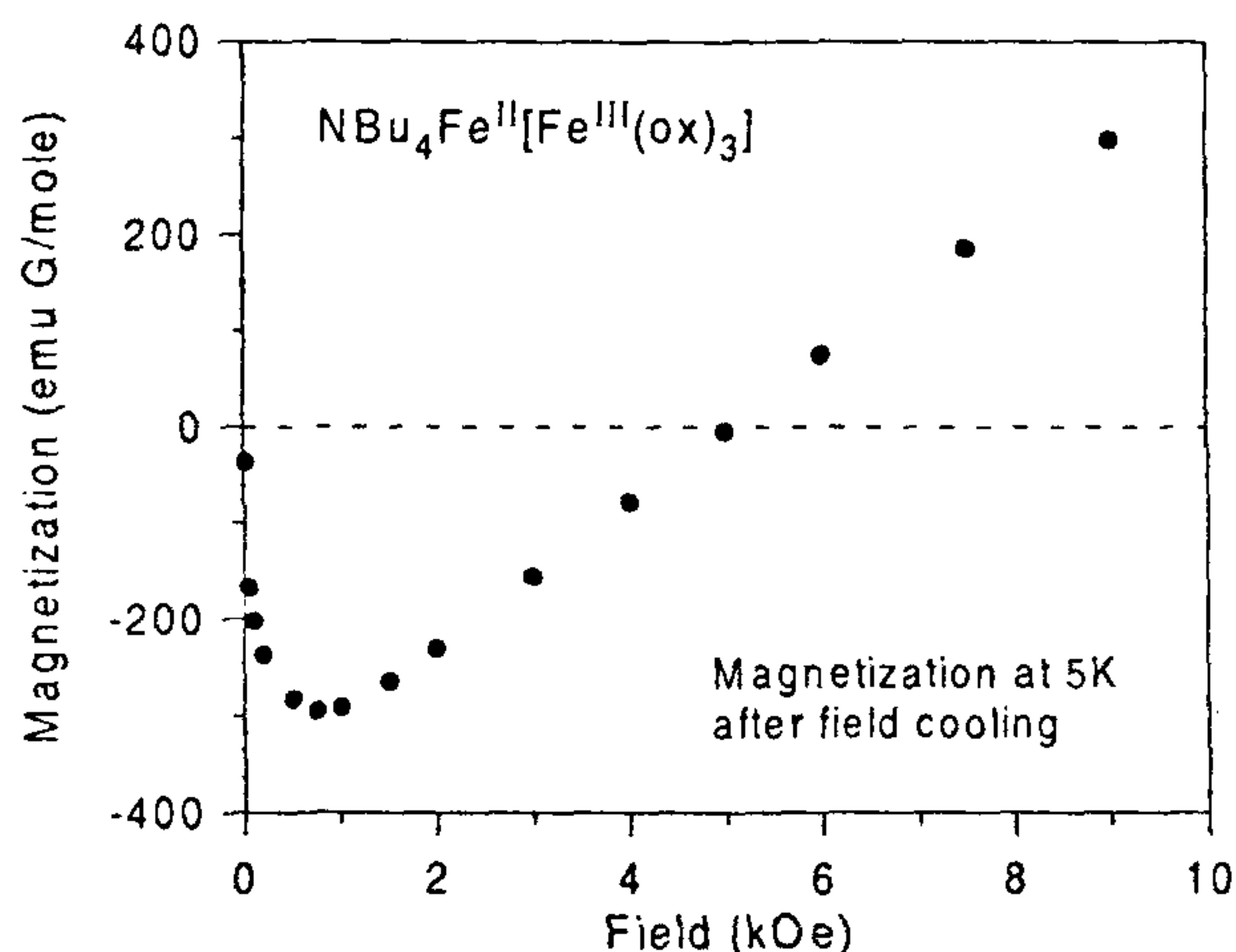


Figure 4. Plot of magnetization at 5 K after field-cooling vs magnetic field for $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$.

of $-380 \text{ emu.G.mol}^{-1}$. From this value the difference of the two sublattice magnetizations of Fe^{II} and Fe^{III} at 5 K can be estimated to be $-0.07 \mu_B$. This value at 5 K is rather small, given that the Fe^{II} and Fe^{III} ions are both in their high-spin states²², $S=2$ and $S=5/2$ respectively, resulting in a theoretical difference of their saturation moments of $1 \mu_B$. Apparently, only less than one-tenth of the expected saturation magnetization is observed in the present sample.

Finally, the hysteresis curve after FC in 1 kOe, measured up to 55 kOe, is shown in Figure 5. The curve exhibits only a weak hysteresis. In the ZFC data, a small remnant magnetization of $150 \text{ emu.G.mol}^{-1}$ is observed (not shown), corresponding to a magnetic moment of $0.027 \mu_B$. The overall behaviour of the FC data is similar to the ZFC behaviour, however, the FC curve is asymmetric, the center of the curve being shifted to negative magnetization values by $-250 \text{ emu.G.mol}^{-1}$. An asymmetry in the FC hysteresis loop is usual for a compound showing the negative magnetization effect after field-cooling¹⁶, but it is surprising that even a magnetic field as large as 55 kOe is not sufficient to destroy the memory of cooling in an applied field.

Thus, a rarely occurring negative magnetization phenomenon is observed in molecular-based magnetic material $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$ in the field-cooled mode only under applied magnetic fields smaller than 5 kOe. This could be because the Zeeman energy competes more effectively with the ordering energy in higher applied magnetic fields, and at some point rotates the spins that give a negative sublattice magnetization in the direction of the applied magnetic field. The absolute value of the saturation magnetization $= 0.07 \mu_B$ was estimated from the field dependence of the FC magnetization at 5 K. The memory of the FC procedure cannot be destroyed by a magnetic field of 55 kOe. A

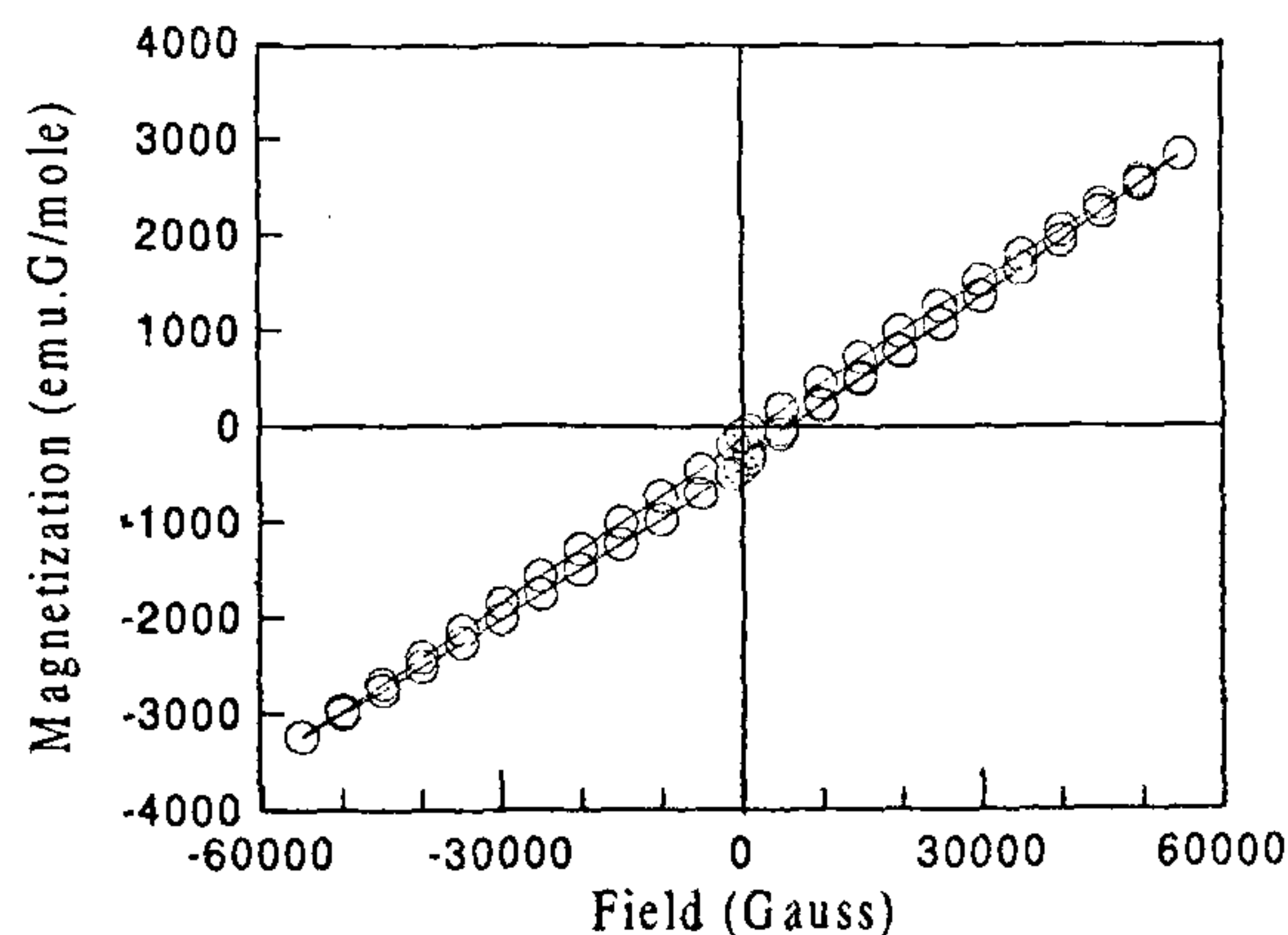


Figure 5. Hysteresis curve at 5 K after field-cooling under 1 kOe magnetic field for $\text{NBu}_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$.

detailed understanding of the observed anomalous behaviour in this compound requires more accurate knowledge of the various magnetic interactions than is presently available. This information can be obtained by a neutron diffraction study.

1. Kahn, O., in *Molecular Magnetism*, VCH, New York, 1993.
2. in Proceedings of the International Conference on Molecule-Based Magnets; *Mol. Cryst. Liq. Cryst.*, 1995, pp. 271–274.
3. Tamaki, H., Zhong, Z. J., Matsumoto, N., Kida, S., Koikawa, M., Achiwa, N., Hashimoto, Y. and Okawa, H., *J. Am. Chem. Soc.*, 1992, **114**, 6974.
4. Okawa, H., Matsumoto, N., Tamaki, H., Kida, S. and Ohba, M., *Mol. Cryst. Liq. Cryst.*, 1993, **233**, 257.
5. Reiff, W. M., Kreis, J., Meda, L. and Kirss, K. U., *Mol. Cryst. Liq. Cryst.*, 1995, **273**, 181.
6. Bhattacharjee, A., Iijima, S. and Mituzami, F., *J. Magn. Magn. Mater.*, 1996, **153**, 235.
7. Nutall, C. J., Bellitto, C. and Day, P., *J. Chem. Soc., Chem. Commun.*, 1995, 1513.
8. Benard, S., Yu, P., Coradin, T., Riviere, E., Nakatani, K. and Clement, R., *Adv. Mater.*, 1997, **9**, 981.
9. Atovmyan, L. O., Shilov, G. V., Lyubovskaya, R. N., Zhilyaeva, E. I., Ovanesyan, N. S., Pirumova, S. I. and Gusakovskaya, I. G., *JETP Lett.*, 1993, **58**, 317.
10. Decurtins, S., Schmalte, H. W., Oswald, H. R., Linden, A., Ensling, J., Gutlich, P. and Hauser, A., *Inorg. Chim. Acta.*, 1994, **216**, 65.
11. Carling, S. G., Mathoniere, C., Day, P., Malik, K. M. A., Coles, S. J. and Hursthouse, M. B., *J. Chem. Soc., Dalton Trans.*, 1996, 1839.
12. Pellaux, R., Schmalte, H. W., Huber, R., Fischer, P., Hauss, T., Ouladdiaf, B. and Decurtins, S., *Inorg. Chem.*, 1997, **36**, 2301.
13. Mathoniere, C., Carling, S. G., Yusheng, D. and Day, P., *J. Chem. Soc., Chem. Commun.*, 1994, 1551.
14. Mathoniere, C., Nutall, C. J., Carling, S. G. and Day, P., *Inorg. Chem.*, 1995, **35**, 1201.
15. N'eel, L., *Ann. Phys. (Leipzig)*, 1948, **3**, 137.
16. Menyuk, N., Dwight, K. and Wickham, D. G., *Phys. Rev. Lett.*, 1960, **4**, 119.
17. Standley, K. J., in *Oxide Magnetic Materials*, Oxford University Press, Oxford, 1972, Second edition.
18. Shirakawa, N. and Ishikawa, M., *Jap. J. Appl. Phys.*, 1991, **30**, L755.
19. Mahajan, A. V., Johnston, D. C., Torgeson, D. R. and Borsa, F., *Phys. Rev.*, 1992, **B46**, 10966.
20. Hur, N. H., Kim, S. H., Yu, K. S., Park, Y. K., Park, J. C. and Kim, S. J., *Solid State Commun.*, 1994, **92**, 541.
21. Okashi, S., Sato, O., Iyoda, T., Fujishima, A. and Hashimoto, K., *Inorg. Chem.*, 1997, **36**, 268.
22. Iijima, S., Katsura, T., Tamaki, H., Mitsumi, M., Matsumoto, N. and Okawa, H., *Mol. Cryst. Liq. Cryst.*, 1993, **233**, 263.

ACKNOWLEDGEMENTS. This work was carried out during A. Bhattacharjee's stay at Hahn-Meitner-Institut (HMI), Germany, as Guest Scientist. We thank Prof. M. Steiner, Director, BENSC, HMI, for his interest in this work.

Received 3 September 1998; accepted 10 November 1998

Quantification of pollutant migration in the groundwater regime through mathematical modelling

M. Thangarajan

National Geophysical Research Institute, Hyderabad 500 007, India

The process of groundwater pollution is a complicated one and quite different from that of surface water pollution. In the case of surface water, the pollution is rapid and involves only short-term process. In contrast, the pollutant in the case of groundwater, may take a very long time to reach the saturated zone and get mixed with native water. It is, generally, accepted that groundwater pollution is irreversible, i.e. once it is polluted, it is difficult to restore the original water quality in a short span of time. It is, therefore, necessary to quantify the pollutant migration in the groundwater regime and take appropriate remedial measures to restore the aquifer system. Mass transport modelling technique has been proved to be a potential tool to study the pollutant migration. Finite difference technique coupled with the method of characteristics has been widely applied for quantification of pollutant migration. Besides outlining the salient principles of mass transport modelling, the use of this technique has been illustrated in the upper Palar river basin (Tamil Nadu) where groundwater has been polluted in about 200 km² due to discharge of untreated tannery effluents. The study has explicitly brought out that if tannery effluents continue to be discharged at the present level, the groundwater pollution will continue to increase both in volume and concentration.

THE increasing demand for water to meet domestic, industrial and agricultural needs is placing great emphasis on the development of groundwater resources. The over-exploitation of groundwater resources in some parts of the country induces degradation of groundwater quality as well as the discharge of untreated effluents, adding contaminants to the groundwater system. The pollution of groundwater regime is not only due to sub-surface waste disposal, but is also attributable to the seepage of contaminants from rivers and lakes, impoundment of toxic waste on unlined surfaces, indiscriminate spraying of insecticides, pesticides and excessive use of chemical fertilizers, etc. The pollutant mass migrates with the groundwater flow and manifests itself even at places where one least expects any contamination. It is, therefore, imperative to study the movement of contaminants in an aquifer so as to predict their migration and work out suitable remedial measures. Based on a well-planned network for collection of geohydrological and hydro-chemical data, a deterministic numerical model of mass transport in groundwater regime may be prepared which can help assess the rate and extent of pollutant migration.