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Variable temperature electron paramagnetic resonance investigations of a kerosene-based magnetic fluid

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Abstract

The kerosene-based ferrofluid RP-90 has been examined by electron paramagnetic resonance (EPR) from room temperature to liquid nitrogen temperature at the X-band frequency 9.41 GHz. The variations in the g-value and (ΔH) with temperature indicate the presence of a magnetic phase transition from a ferromagnetic to a 'spin glass or cluster glass' state. This transition is associated with the freezing point of the carrier medium. No evidence of the presence of superparamagnetism was observed. The linewidth variation with temperature indicates a dominant bulk rotation relaxation mechanism (τ_B).

Keywords: Magnetic fluid; Electron paramagnetic resonance; Rotation relaxation

1. Introduction

A ferrofluid is a colloidal dispersion of single-domain magnetic particles of Fe_3O_4 (size 10–100 Å) in a fluid medium such as water, diester, paraffin, kerosene, etc. In the absence of an applied magnetic field each particle attracts other neighbouring particles by means of dipole–dipole interactions in the direction of the magnetic moment and forms a chain-like cluster in certain magnetic fluid [1]. However, in the presence of a field the magnetic moment aligns with the applied magnetic field direction by two distinct mechanisms: (1) the bulk rotation of particles with the magnetic moment locked in the easy direction of magnetization, and (2) the rotation of the magnetic vector out of the easy direction. The former process has a relaxation time given by

$$\tau_B = 3V\eta/kT, \qquad (1)$$

where η is the viscosity of the carrier fluid, V is the volume of the particle, k is the Boltzmann constant and T is the absolute temperature. The latter process, known as Néel rotation, has a relaxation time behaviour given by

$$\tau_N^{-1} = f_0 \exp[-KV/kT], \qquad (2)$$

where K is the effective anisotropy constant of the particles, and f_0 has a dimension of the frequency and a value $\sim 10^9$ s^{-1}. The Néel relaxation is a rapidly varying function of the particle diameter D

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($V = \pi D^3/6$) compared to τ_B. Particles with sizes less than a critical diameter exhibit superparamagnetic behaviour, and follow the Néel relaxation mechanism. However, a ferrofluid contains a distribution of particle sizes, 10–100 Å, so that both mechanisms contribute to the value of the magnetization. O'Grady et al. [2] used the dominant mode of magnetization in a ferrofluid.

In the present paper we report the results of electron paramagnetic resonance (EPR) investigations of kerosene-based magnetite as a solid phase ferrofluid. This work was carried out with a view to understanding the relaxation behaviour and the phase transition present in a ferrofluid.

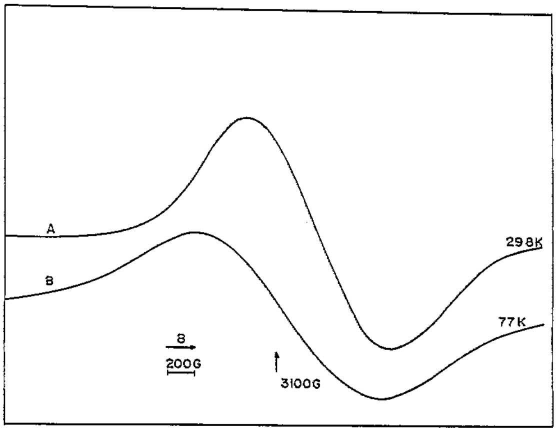

Fig. 1. X-band spectra of the kerosene-based ferrofluid RP-90 at (A) 298 K and (B) 77 K.

2. Experimental

Laboratory prepared magnetic fluid RP-90 of ultrafine single-domain magnetic particles of size ~ 100 Å suspended in kerosene were investigated [3]. The EPR spectra of the magnetic fluid were recorded on a Bruker ESP-300 EPR spectrometer operating at X-band frequencies kHz field modulation and phase sensitive detection to obtain the first derivative EPR signal. DPPH ($g = 2.0036$) was used as a field marker. The low-temperature spectra were recorded using an ER 4111 variable temperature accessory. The EPR spectra were recorded at variable temperatures (77–298 K) using liquid nitrogen accessories.

3. Results and discussion

The EPR spectra of the kerosene-based ferrofluid RP-90 showed single broad signals in the temperature range 77–298 K, as shown in Fig. 1. Fig. 2 shows the variation in the linewidth (ΔH) with temperature (T). ΔH increases monotonically with decreasing temperature. However, in the temperature range 260–200 K the increase in ΔH is very steep. Similar ΔH behaviour was observed earlier by Patel et al. [4] in the diester and water-based magnetic fluids DOA-12, AS-25, AM-05 and LS-35.

The dimensionless parameter g is defined as a proportionality constant between the frequency and the field at which resonance occurs. Fig. 3 shows the variation in the g-value with temperature for the kerosene-based magnetic fluid. Initially, g decreases with decreasing temperature up to 205 K, and then increases with further lowering in temperature up to 77 K. The variation of the linewidth and g with temperature indicates that the kerosene-based ferrofluid RP-90 undergoes a magnetic phase transition at around 205 K [5]. It is interesting to note that the freezing point of the carrier liquid kerosene is 240 K.

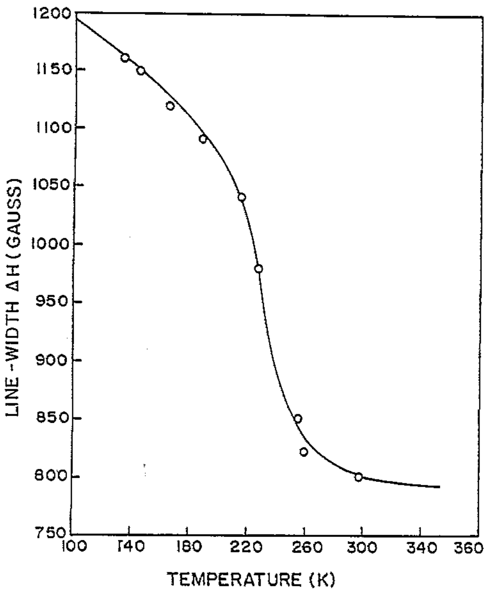

Fig. 2. Variation of the linewidth (ΔH) as a function of temperature for the kerosene-based ferrofluid. O ΔH values; — trend.

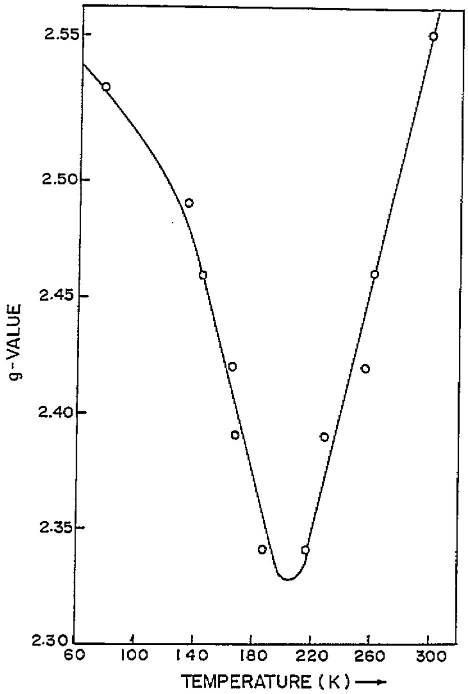

Fig. 3. Variation of g-values for the kerosene-based ferrofluid as a function of temperature. ○ g-values; — trend.

These results reveal that the magnetic phase transition is associated with the freezing of the carrier liquid. More clearly, at room temperature all the spins in the kerosene-based ferromagnetic fluid can be imagined to adopt a unidirectional orientation under the influence of an applied magnetic field. At this stage the carrier liquid kerosene does not exert any force that can affect the unidirectional alignments of the spin. The higher g-value and smaller linewidth may be due to this alignment of spins. However, upon lowering the temperature the viscosity of the carrier liquid begins to increase, which improves the bulk rotation mechanism, and at a particular temperature (240 K) the kerosene freezes. In the temperature range below 240 K, the viscosity is very high because the moments of the majority of particles are 'blocked'. Once the sample is frozen the viscosity remains constant due to the blocking of the moments. It is clear that in the sample the dominant mode of viscosity is via bulk rotation. The freezing of kerosene leads to the simultaneous freezing of the spins in whatever random direction they existed. The initiation of process of freezing of the carrier liquid at any localized site in the body of the ferrofluid can cause local contraction, which in turn causes the de-alignment of the spins. Ultimately, this leads to randomness in the spin orientation. The new state is known as a 'spin glass or cluster glass state' [6].

The anisotropic fields arising from the randomly organized spins lead to lower a g-value and a broader linewidth. In essence, when dynamic phenomena are considered, the freezing process leads to a slowing down of the spin fluctuations, which in turn causes slower relaxation processes. The observed initial behaviours of g and ΔH are obviously due to the freezing of the carrier liquid.

With further reductions in temperature to below 205 K, the g-value increases and the increase in ΔH values slows down. We believe that this takes place

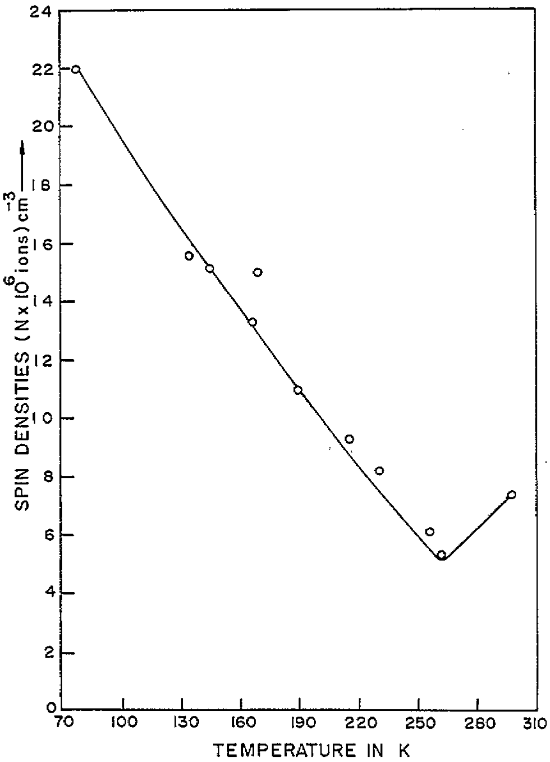

Fig. 4. Concentration of isolated spins N as a function of temperature for the ferrofluid. ○ estimated spins; — trend.

through the spin-glass to cluster glass transition. This state is characteristic of re-entrant magnetism [7,8]. In this case the spins freeze in random directions and give rise to random anisotropy fields that in turn broaden the EPR signal. This may be due to the growth of individual cluster chain formation (bulk rotation mechanism) which enhances the susceptibility of the system. Similar observations were also noted by O'Grady et al. [2] in the initial susceptibility of the system. The linewidth increases as the temperature is further reduced from 205 K, and the g-value increases. Further, the exchange field is also temperature dependent. Below 205 K the dipole–dipole interaction leads to further ordering of the spins and consequently the internal exchange field increases. Therefore, the decrease in temperature below 205 K results in increased g-values. Hence, the variations in the linewidth and g-value with temperature indicate that the interparticle ferromagnetism of the colloidal chain is disrupted at 205 K and spin freezing takes place. Fig. 4 shows the estimated concentration of isolated spins N as a function of temperature.

Sharma and Waldner [9] and Kneller [10] observed a narrow signal with a broad ferromagnetic resonance similar to what is attributed to the so-called superparamagnetism. However, Shliomis and Raikher [11] interpreted this narrow signal as being due to the presence of free radical impurities. In the present investigation we observed no such lines, although the variation in the linewidth indicates a dominant bulk rotation mechanism for the magnetic moment in the present system.

4. Conclusions

Our variable temperature EPR investigations of a kerosene-based magnetic fluid have indicated the presence of a magnetic phase transition in the system from ferromagnetism to a 'spin glass or cluster glass state' at lower temperatures. The linewidth and the spin concentration indicate a bulk rotation mechanism.

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References

[1] S. Chikazumi, S. Taketomi, M. Ukita, M. Mizukami, H. Miyajima, M. Setogawa and Y. Kurihara, J. Magn. Magn. Mater. 65 (1987) 245.
[2] K. O'Grady, J. Popplewell and S.W. Charles, J. Magn. Magn. Mater. 39 (1983) 56.
[3] R.P. Pant, Ph.D. Thesis, Bhavnagar University, 1993.
[4] J.M. Patel, S.P. Vaidya and R.V. Mehta, J. Magn. Magn. Mater. 65 (1987) 273.
[5] A. Taylor, Introduction to X-ray Metallography (Wiley, New York, 1961) p. 885.
[6] D.W. Moon, J.M. Aitken and R.K. MacCrone, Phys. Chem. Glasses 16 (1975) 91.
[7] S. Morup, J. Magn. Magn. Mater. 37 (1983) 39.
[8] D.C. Matlis, The Theory of Magnetism II (Springer, Berlin, 1985) p. 57.
[9] V.K. Sharma and F. Waldner, J. Appl. Phys. 48 (1971) 4298.
[10] F. Kneller, J. Appl. Phys. 39 (1968) 945.
[11] M.I. Shliomis and Y.U.L. Raikher, IEEE Trans. Magn. 17 (1980) 273.