MATERIALS CHEMISTRY COMMUNICATION

Magneto-optical properties of nanostructured iron

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Particles of α-iron of 2–10 nm size have been prepared by chemical synthesis, stabilized and dispersed into a polymer matrix. The composite was characterized using high-resolution transmission electron microscopy. The optical Faraday rotation of the polymer composite, measured at 633 nm, was approximately 1.2° T^{-1}. The Verdet constant measured by the Faraday rotation of the polymer composite at 633 nm is 0.36 min Oe^{-1} cm^{-1}.

Nanostructured materials[1] are those with a grain or domain size of less than 100 nm. This significant reduction in size can produce dramatic changes in the behaviour of the material. Because of its high coercivity,[2] iron is often used in magnetic applications. By using nanostructured iron, the efficiency of magneto-caloric refrigeration and magnetic data storage can be improved.[3]

Conventional iron, with larger (μm-sized) domains, is usually prepared by physical routes such as arc melting.[4] Nanostructured materials are also prepared by physical methods, including sputtering and molecular beam epitaxy (MBE).[5] However, there has recently been much interest in the chemical synthesis of nanostructured materials. This approach has the advantages of improved mixing, better control of stoichiometry, and tailored synthesis by assembly of atomic or molecular precursors.[6]

Iron nanoparticles, either as a solid or incorporated into an amorphous matrix, have been shown to exhibit superparamagnetism at low temperatures.[7] Owing to the small size of the nanoparticles the cooperative behaviour of the spins does not lead to ferromagnetism. At room temperature the composite material has paramagnetic behaviour. It is of interest to examine the possibility of using nanoparticles of iron and iron oxide in a polymer matrix for use as a Faraday rotator. Iron-containing ferrites such as yttrium iron garnet and bismuth iron garnet are already used as Faraday rotators for optical isolator applications.[8] The possibility of a polymeric Faraday rotator using nanoparticles which can be moulded or cast into rods without the expense of crystal growth and polishing is very attractive. We have therefore made measurements of the Verdet constant of nitrogen-passivated iron particles in a poly(methyl methacrylate) (PMMA) matrix at 633 nm and 1.3 μm.

Nanostructured iron powder was prepared by thermal decomposition[9] of $Fe(CO)_5$ in decalin solution. During the decomposition and cooling of the mixture, anhydrous ammonia gas was passed through the solution. The magnetic moment of the iron powder was 60 emu g^{-1} (cgs, Gaussian) at room temperature and 120 emu g^{-1} at 10 K.

To prepare the polymer–matrix composite, approximately 500 mg of the powder and 2 ml of dodecanethiol were sealed in a flask under nitrogen and sonicated in a cleaning bath for 2 h. The thiol was then decanted and methyl methacrylate was added, along with azoisobutyronitrile, an initiator. This mixture was polymerized by heating at 72 °C for 2 h.

The composite sample was examined using a JEOL-4000EX electron microscope with an accelerating voltage of 400 kV and a point-to-point resolution of approximately 1.7 Å. HRTEM images were obtained at optimum (Scherzer) defocus. Computer filtering was used to improve the images.

The HRTEM characterization (Fig. 1) of the particles in the PMMA matrix showed that the size distribution is narrow. Symmetry analysis and measurement of the lattice fringe spacings (Fig. 2) in the HRTEM image indicate that the particle is α-Fe (bcc) observed along the ⟨001⟩ zone axis. Particles show flat surfaces, terminating with {110} facets. This seems reasonable, since the (110) planes are most dense in a bcc lattice, which makes them very stable. Surprisingly, the particles were not oxidized. XPS results indicate that nitrogen is present, with a 15:2 iron:nitrogen ratio. It seems likely that nitrogen is on the particle surface, preventing oxidation. However, this is difficult to confirm through TEM because of nitrogen's weak scattering intensity and further studies using NMR and EXAFS are under way.

The magnetic susceptibility of the composite material was

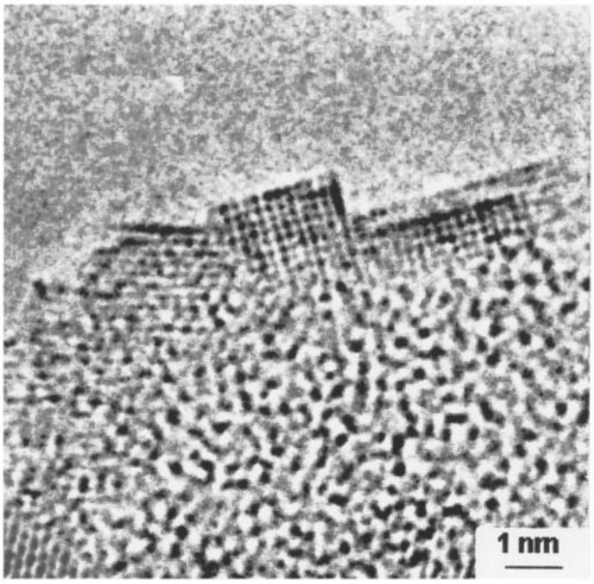

Fig. 1 High-resolution transmission electron microscope image of nanostructured iron/PMMA composite

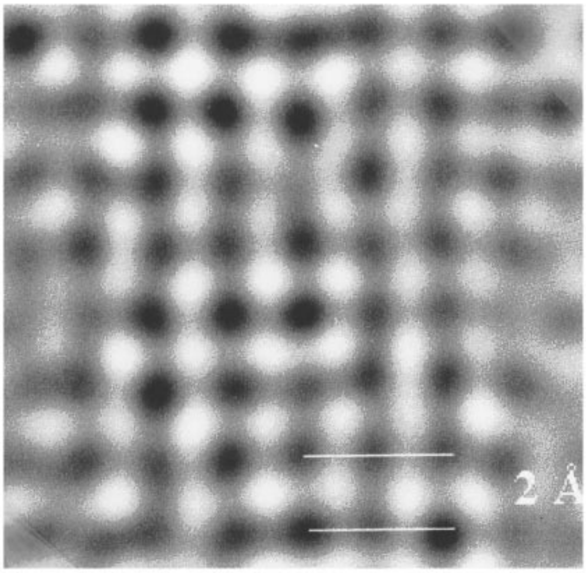

Fig. 2 Computer filtered image of the iron nanoparticle. Black corresponds to atomic columns. Enlargement of nano-Fe HRTEM image.

measured in a Guoy susceptibility balance at room temperature and found to be 1.2×10^{-5} esu. The PMMA matrix has a diamagnetic contribution to the Verdet constant (V_d) while the iron nanoparticles at room temperature have a paramagnetic contribution (V_p). The Verdet constant at fixed temperature T and wavelength λ is given by

$$V(\lambda,T)=V_p(\lambda,T)+V_d(\lambda,T)$$

Magneto-optical experiments were conducted on the samples in the transmission geometry. A polarized laser beam at the desired wavelength (0.633 or 1.3 µm) was transmitted through a sample of the composite material and was collinear with the direction of the applied magnetic field. The magnetic field strength was varied from 0 to 1.5 T. The output polarizer P was oriented at an angle of 45° to the direction of the input polarization. Therefore, if the polarizer is aligned in the direction of the input polarization ($I_{out}=I_o \cos^2 \theta$), the transmission without an applied magnetic field is half the output intensity value. The application of a magnetic field results in a change of the output intensity which is proportional to the rotation of the plane of polarization of the output beam with respect to the input polarization. For small rotations, the change in relative output intensity is equal to the rotation of the plane of polarization in radians. The slope of this curve gives the value of the Verdet constant of the composite material. At 633 nm the transmission of a 200 µm sample is 5%. The losses may be due to a combination of absorption and scattering and no attempt has been made to minimize them at this stage.

Fig. 3 shows the magnitude of rotation of the plane of polarization of the output beam with the applied field at 633 nm. The best linear fit to the data passing through the origin gives a slope of $1.2°\,T^{-1}$. The scatter in the data points give an uncertainty of 10% in the slope and consequently the Verdet constant. The Verdet constant calculated from the slope in units most often quoted in the literature is 0.36 min $Oe^{-1}\,cm^{-1}$. The transmission at 1.3 µm is about 40% in a 500 µm thick sample. The value measured at 1.3 µm from a 500 µm thick sample is 0.1 min $Oe^{-1}\,cm^{-1}$. The drop in Verdet constant at 1.3 µm is theoretically expected. In paramagnetic materials at wavelength far from resonance the Verdet constant decreases as $1/\lambda^2$.

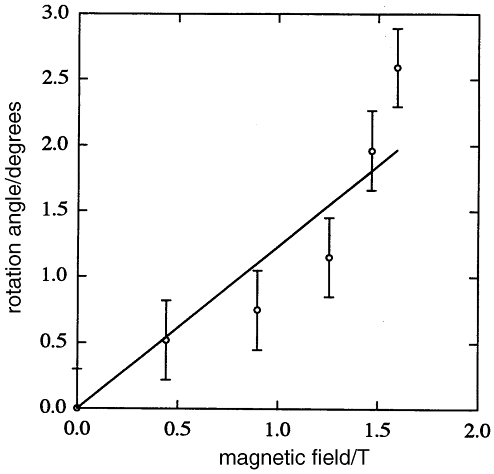

Fig. 3 Faraday rotation as a function of magnetic field

It is interesting to note that at room temperature the Verdet constant at 1.3 µm is considerably larger than the commercially available Faraday rotator glass[10] Hoya FR-5. A uniform dispersion was obtained and phase separation can be avoided by surface functionalization. This approach can be applied to other ferromagnetic or ferrite nanoparticles. Also, nanoparticulate rare-earth-metal trifluorides[11] may be investigated. The polymeric–Fe composite material has not been optimized for its Faraday rotation and scattering losses. These issues need to be further investigated before the polymeric composite material can emerge as an inexpensive alternative to existing inorganic single crystals or glasses. Nevertheless the values of Verdet constant possible in polymeric composites are encouraging.

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