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Magnetic susceptibility and Faraday rotation in zirconium based fluoride glasses

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Abstract. The temperature dependences of the d.c. magnetic susceptibility and Verdet constant in two zirconium based fluoride glasses have been studied. One sample has as a minor constituent dysprosium which has a large magnetic moment that dominates the material's magnetic character. The second sample, containing a small amount of europium, shows both Van Vleck paramagnetism and a Curie–Weiss behaviour. The Curie–Weiss character is believed to come from small amounts of Zr^{3+} and/or Zr^{2+} produced during the sample's manufacturing process. An upper limit is placed on the amount of magnetic zirconium in the material.

1. Introduction

We have been studying the magnetic properties of zirconium based fluoride glasses that contain small amounts of rare earths. Earlier studies of these systems, using Rayleigh–Brillouin light scattering and Faraday rotation [1, 2] suggest that they may enter a spin glass state at pumped liquid helium temperatures. This investigation focuses on the temperature dependence of the Faraday rotation and static magnetic susceptibility within these materials. The compositions of the samples under discussion, in mole per cent, are given in table 1.

Table 1. Mole per cent composition of ZBDyA and ZBLAEu samples.

	ZrF_4	BaF_2	LaF_3	AlF_3	EuF_3	DyF_3
ZBLAEu	57	34	3	4	2	—
ZBDyA	57	34	—	4	—	5

Faraday rotation occurs when plane polarized light is passed through a sample parallel to the direction of an applied magnetic field. The linearly polarized light is a superposition of two circular polarizations, one rotating clockwise and the other counterclockwise when viewed along the direction of propagation. The application of a magnetic field removes the degeneracy of the resonant frequencies for the two circular polarizations. This results in a difference between their indices of refraction. As a result, one circular polarization will

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more rapidly pass through the material. When both polarizations emerge from the far end of the sample the recombined plane wave will have its plane of polarization rotated with respect to that of the incident light. More detailed explanations of Faraday rotation may be found in the literature [3–8].

The classic equation for Faraday rotation is:

$$\Theta = VlB \tag{1}$$

where l is the length of the sample and B, the strength of the magnetic field. The constant of proportionality, V, is called the Verdet constant. In the case of paramagnetic material the Verdet constant is given by the equation [9]:

$$V = 4\pi^2\omega^2 \frac{\chi_m}{g\beta ch} \sum_{ij} \frac{C_{ij}}{\omega^2 - \omega_{ij}^2} \tag{2}$$

where g is the Landé factor; β, the Bohr magneton; c, the speed of light; h, Planck's constant, and ω, the angular frequency of the light. The terms C_{ij}, and ω_{ij}, are measures of the transition probability and energy splitting between the ground and excited states respectively. The term χ_m, is the d.c. magnetic susceptibility of the sample which is given by the Curie–Weiss law:

$$\chi_m = Np^2 \frac{\beta^2}{3k_B} \frac{1}{(T - T_c)} \tag{3}$$

where N is the number of paramagnetic atoms in the sample; p, the effective Bohr magneton number; k_B, the Boltzmann constant; T the temperature of the sample and T_c the critical temperature. Therefore measurements of Faraday rotation and magnetic susceptibility allow us to examine both magnetic and electronic properties of a sample.

Measurements of the Verdet constant were carried out at SUNY Brockport and at Rensselaer Polytechnic Institute. The equipment used to make these measurements is discussed in the next section.

The d.c. magnetic susceptibility of the samples was measured using two different techniques. A SQUID magnetometer was used to measure the susceptibility of the ZBLAEu sample. These measurements were performed by Dr Chen Tsui at IBM's T J Watson Laboratories. The susceptibility of ZBDyA was measured at Rensselaer Polytechnic Institute using a vibrating sample magnetometer. In both of these experiments the susceptibility was determined from measurements of the bulk magnetization. In the case of the vibrating sample magnetometer, the magnetic field was swept to 10 kG. Descriptions of SQUID and vibrating magnetometer systems may be found elsewhere [10].

2. Experimental set-up

Faraday rotation was measured using the system shown in figure 1. Mechanically chopped light from a helium–neon laser (632.8 nm) was focused onto the end of a fibre optic. The light fibre carried the unpolarized light to the bottom of the sample chamber, housed within a Janis Helium Research Dewar. The beam was collimated using a fibre optic coupling sphere and then polarized. The light passed through the sample and out of the cryostat. The sample was positioned at the centre of a 10 T superconducting solenoid. The temperature of the sample was monitored with a carbon-glass resistor and maintained with an accuracy of ± 0.05 K. After exiting the cryostat, the polarization of the light was analysed with a Glan–Thompson prism mounted on a stepper motor. The intensity of the light passing through the prism was monitored with a photo-diode. A lock-in amplifier was used to detect the

signal and discriminate it from external noise. Data collection and temperature regulation was computer controlled. A detailed discussion of the equipment may be found elsewhere [11].

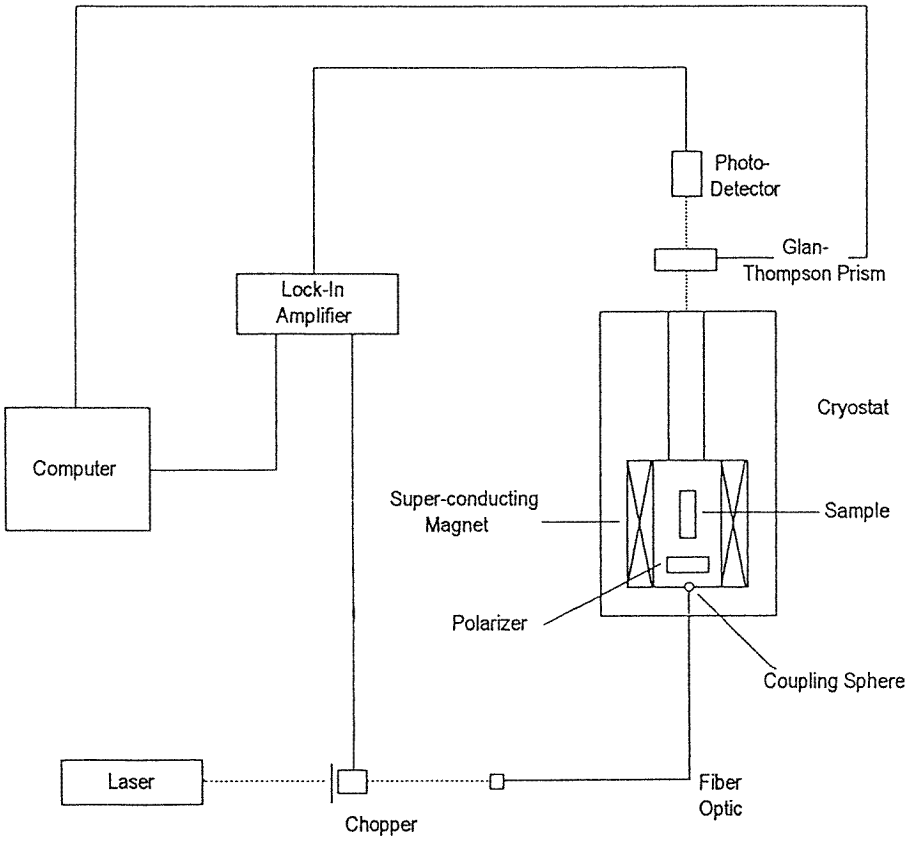

Figure 1. Block diagram of the Faraday rotation experimental set-up.

In order to determine the Verdet constant of the samples, two measurements of the light intensity as a function of Glan–Thompson prism orientation were made. In one measurement, the sample was subjected to an applied magnetic field of 3.0 kG. In the other, the applied field was zero. Both sets of data were fit to a cosine-squared curve using Mathematica and their extinction angles were determined. The difference between the extinction angles of these measurements gives the Faraday rotation, Θ, from which the Verdet constant was calculated.

3. Results (ZBDyA)

The Verdet constant was measured, as a function of temperature, between 120 K and 2 K. As the temperature of the sample is lowered, the size of the Verdet constant shows a marked increase. At 2 K the value for the Verdet constant is 30 times that at 120 K. See table 2. Because the Verdet constant is proportional to the magnetic susceptibility, we should expect that it follows the Curie–Weiss law, provided that the sample is in a paramagnetic state. In

figure 2 the inverse of the Verdet constant is plotted against temperature. The results show a linear relationship consistent with a paramagnetic system. A least squares fit to the data gives a temperature intercept of −1.3 K, indicating a tendency for anti-ferromagnetic interactions between magnetic moments. Upon extrapolation of the data to room temperature, a Verdet constant of −0.0229 min G^{-1} cm^{-1} (±0.0006 min G^{-1} cm^{-1}) is found. After corrections to the data of Letellier *et al* [12], to account for concentration differences, we find a room temperature Verdet constant for Dy^{3+} of −0.0228 min G^{-1} cm^{-1}, in excellent agreement with ours.

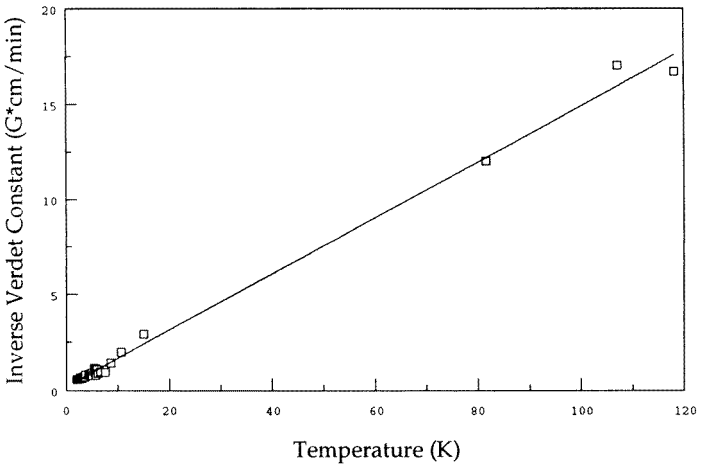

Figure 2. The inverse Verdet constant as a function of temperature for ZBDyA. A fit of the data shows that the temperature axis intercept is −1.3 K, consistent with the presence of antiferromagnetic interactions.

Table 2. Values for the Verdet constant of ZBDyA between 2 K and 120 K.

T (K)	V (min G^{-1} cm^{-1})	T (K)	V (min G^{-1} cm^{-1})	T (K)	V (min G^{-1} cm^{-1})
118.2	−0.0599	5.64	−0.8993	3.11	−1.5052
107.2	−0.0587	5.46	−1.0870	3.09	−1.5220
81.63	0.0831	5.42	−0.8689	2.99	−1.4747
15.00	−0.3442	5.01	−1.3035	2.92	−1.5997
10.60	−0.5056	4.86	−1.0944	2.86	−1.6140
8.62	−0.7037	4.63	−1.2329	2.78	−1.5157
7.47	−1.0649	4.53	−1.2979	2.65	−1.5872
7.45	−0.9241	4.28	−1.2370	2.64	−1.5358
6.61	−1.0386	4.27	−1.1506	2.42	−1.6689
6.13	−1.1263	3.74	−1.2323	2.37	−1.7099
5.90	−0.9405	3.61	−1.4227	2.20	−1.7458
5.67	−1.2954	3.31	−1.3928	2.03	−1.8138

D.C. magnetic susceptibility measurements were made over the temperature range 5 K to 250 K. The measurements were calibrated using a nickel standard. The inverse susceptibility is plotted as a function of temperature in figure 3. From the linearity of this graph it is apparent that ZBDyA follows the Curie–Weiss law. The data were fitted, using the method of least squares. From this fit the temperature axis intercept is found to be −76 K, indicating

that anti-ferromagnetic interactions are present in this glass. From the slope of the graph, the effective Bohr magneton number for Dy^{3+} was calculated to be 10.1 ± 0.5. The accepted value of the effective Bohr magneton number is 10.63 [13]. Similar measurements on $0.20BaF_2xDyF_3(0.8-x)NaPO_3$ glass systems ($x = 0.2$ or 0.3) yield an effective Bohr magneton number of 10.65 [12].

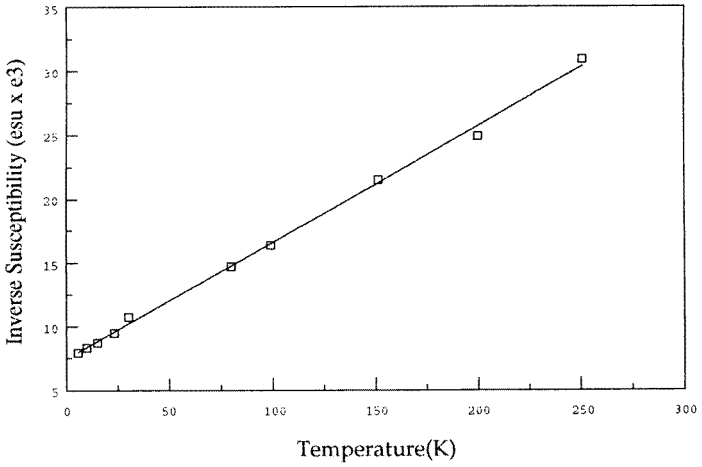

Figure 3. Inverse magnetic susceptibility plotted as a function of temperature for ZBDyA. The line is a least squares fit of the data.

4. Results (ZBLAEu)

The temperature dependence of the Verdet constant for this sample is shown in figure 4. As can be seen, the value of the Verdet constant remains relatively unchanged over the entire temperature range. Examining the electronic structure of ZBLAEu's constituents shows that all except Eu^{3+} are closed shell and should not contribute a paramagnetic signal. Eu^{3+} is one electron short of a half filled 4f shell. As a result this ion should exhibit Van Vleck paramagnetism. Because of the temperature independence of Van Vleck paramagnetism the behaviour of the Verdet constant is reasonable if the Faraday rotation results mainly from Eu^{3+}.

The d.c. magnetic susceptibility of this sample was measured as a function of temperature using a SQUID magnetometer. The results are displayed in figure 5. The plot clearly shows a paramagnetic system with a temperature dependent susceptibility. The temperature independent susceptibility of the Eu^{3+}, χ_{Eu}, was determined from the slope of a plot of χT against T. The value found for χ_{Eu} was 9.379×10^{-7} esu. Using this, the effective Bohr magneton number for Eu^{3+} was determined to be 3.2 ± 0.3, in good agreement with the value of 3.4 reported in the literature [13].

The contribution of Eu^{3+} was then subtracted from the initial data. The results are shown in figure 6. This shows a linear relationship between the inverse susceptibility and the temperature. The results show that the sample is paramagnetic and a fit of the data finds the temperature intercept to be at 0.32 K indicating ferromagnetic interactions between the moments. We believe that this paramagnetic signal results from small amounts of either Zr^{2+} or Zr^{3+} created during the manufacturing of the sample.

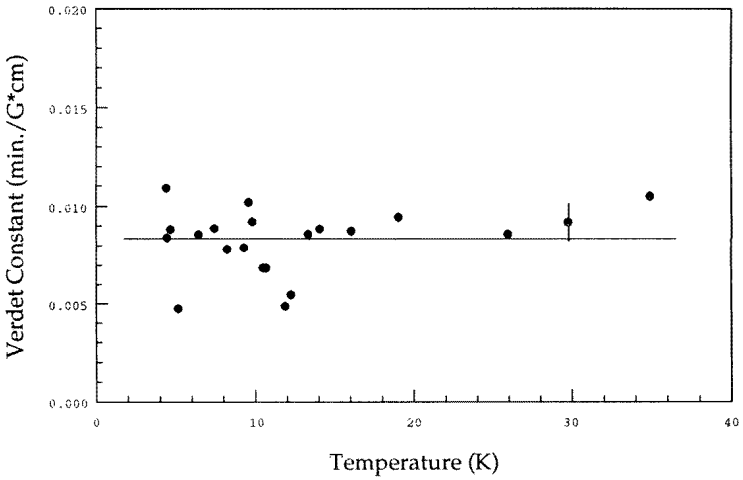

Figure 4. The Verdet constant as a function of temperature for ZBLAEu.

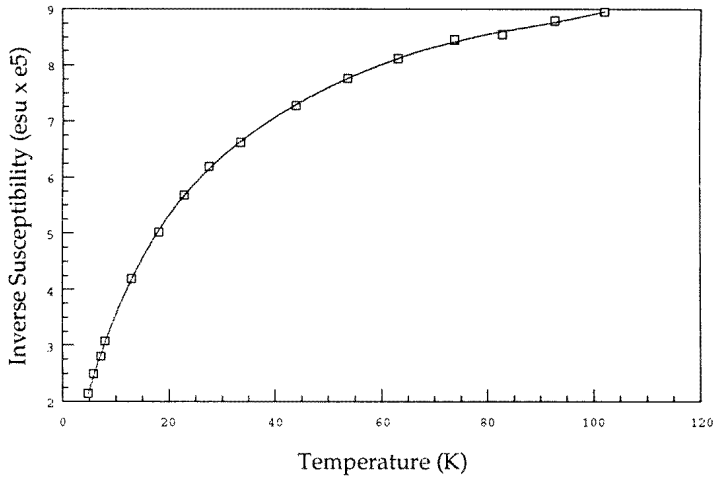

Figure 5. Inverse magnetic susceptibility as a function of temperature for ZBLAEu.

In the fabrication of zirconium fluoride based glass, fluorine atoms are stripped from the zirconium during the melt process. In order to maintain the zirconium in the +4 state, the melt is made with carbon tetrachloride vapour flowing through the furnace. In principle, the carbon tetrachloride will break down and the free chloride will bond with zirconium that has lost fluoride atoms. This reactive atmosphere processing of the melt has been shown to reduce the formation of reduced ZrF_4 particulates. However, it is likely that not all the zirconium is maintained in the +4 state [14].

There are two paramagnetic oxidation states of zirconium, +2 and +3, that can be introduced into the sample through this mechanism. Of the other elements in the glass only europium has an oxidation state other than that implied by the composition formula shown in table 1. If a fluorine atom were stripped from Eu_3F_4 it would leave the europium in the +2 state which is paramagnetic. To test for the presence of Eu^{2+}, Mossbauer effect

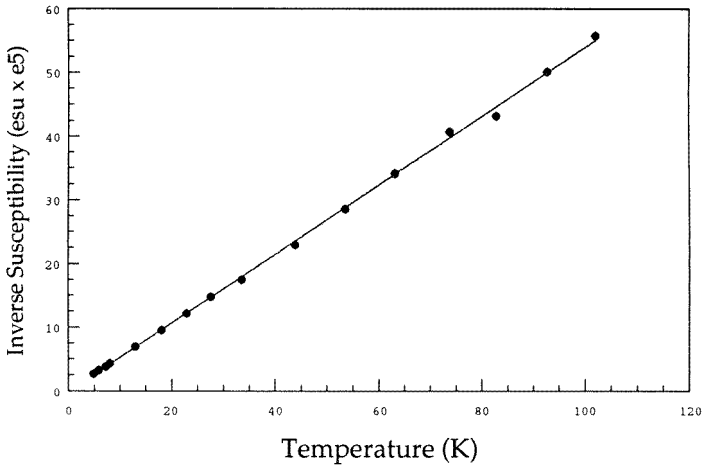

Figure 6. The least squares fit for the inverse magnetic susceptibility of ZBLAEu after the Van Vleck contribution has been removed.

measurements were made on the sample. These measurements showed that there is no Eu^{2+} present in ZBLAEu [15].

Assuming that zirconium is responsible for the temperature dependant magnetic behaviour of ZBLAEu, we can estimate the amount of Zr^{3+} or Zr^{2+} in the sample. From the basic electronic configuration of Zr^{3+} and Zr^{2+}, effective Bohr magneton numbers were calculated for each ion. The room temperature susceptibility of the system was obtained from the fit of the data shown in figure 6. The Curie law was then used to determine the number of magnetic ions in the sample. In order to simplify matters we have assumed that the sample contains either all Zr^{3+} or all Zr^{2+}. In this case the magnetic susceptibility seen in ZBLAEu can be attributed to the presence of either 0.16 atomic per cent Zr^{3+} or 0.10 atomic per cent Zr^{2+} in the sample.

5. Discussion and conclusions

From the data presented it is evident that ZBDyA behaves as a typical Curie–Weiss paramagnet over the temperature range studied. Because dysprosium has a large single ion anisotropy [16], the lack of interactions between moments at these temperatures is not unexpected. The effective Bohr magneton number for Dy^{3+} was found to be 10.1 in agreement with the literature. Extrapolation of the susceptibility data shows that χ^{-1} reaches zero at a temperature of -76 K. Therefore interactions between the Dy^{3+} moments are antiferromagnetic in nature. Both the Verdet constant and the magnetic susceptibility follow a Curie–Weiss temperature behaviour. Upon fitting the data for the Verdet constant and susceptibility we find that, within error, the temperature dependence of the former quantity is entirely accounted for by the Curie–Weiss behaviour of the magnetic susceptibility.

The susceptibility data from ZBLAEu show a system that has both a Van Vleck paramagnetism and a paramagnetism that follows the Curie–Weiss law. From the Van Vleck contribution to the system's susceptibility, an effective Bohr magneton number of 3.2 for Eu^{+3} was found. It is likely that the temperature dependent susceptibility results from small amounts of Zr^{3+} and/or Zr^{2+} formed during the manufacturing of the sample.

Upper limits for the amount of Zr^{3+} and Zr^{2+} were determined to be 0.16 and 0.10 atomic per cent respectively.

Because both Eu^{3+} and paramagnetic zirconium are present in the sample, both could contribute to the Faraday rotation. From equation (2) we see that the strength of each contribution is proportional to the magnetic susceptibility of the ion and the probability of exciting a transition between states within the ion. Since the susceptibility of a Van Vleck paramagnet is temperature independent, if the sum in equation (2) were large for Eu^{3+}, compared to zirconium, then the europium ion would dominate the Faraday rotation. The result would be a Verdet constant that shows little temperature dependence.

To test this hypothesis, room temperature measurements of the Verdet constant in ZBLAEu and its base glass, ZBLA, were performed. The composition of the base glass is $(ZrF_4)_{58}(BaF_2)_{33}(LaF_3)_5(AlF_3)_4$. If Eu^{3+} were primarily responsible for the Faraday rotation then we should expect ZBLAEu to exhibit a larger Verdet constant than ZBLA. This turns out not to be the case. For ZBLAEu we find a room temperature Verdet constant of -0.0052 min G^{-1} cm^{-1} while for ZBLA we find -0.0072 min G^{-1} cm^{-1}. The uncertainty in these values is ± 0.0007 min G^{-1} cm^{-1}. The results indicate that Eu^{3+} does not play a significant role in Faraday rotation within ZBLAEu. Evidently the temperature invariance results from a low probability of exciting transitions within the sample.

Both ZBLAEu and ZBDyA contain the same amount of zirconium and were fabricated using the same technique. Therefore, we should expect comparable amounts of Zr^{3+} and Zr^{2+} in each sample. Yet the magnetic behaviour of ZBDyA can be explained without considering the presence of paramagnetic zirconium. This can be attributed to the larger effective Bohr magneton number of the dysprosium and to the fact that the population of Zr^{3+} and/or Zr^{2+} ions in the sample is about one quarter that of the Dy^{3+}.

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