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THE LOW TEMPERATURE DEPENDENCE OF MAGNETIZATION AND AC SUSCEPTIBILITY OF GLASSY $Fe_{91-x}Zr_7B_2Ni_x$ (x =0,5,10,15) ALLOYS

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Abtract--We have studied the magnetization in fields up to 1T at 5K, the saturation magnetization dependence on temperature and the temperature dependence of AC-susceptibility at very low fields (5mOe to 50mOe) of glassy $Fe_{91-x}Zr_7B_2Ni_x$ (x = 0, 5, 10, 15) alloys. The temperature dependence of the magnetization follows the predictions of spin wave excitations with long wavelengths. At zero Ni concentration there is a clear competition between ferromagnetic and antiferromagnetic interactions giving rise to spin-glass behaviour. The addition of Ni drastically modifies the magnetic properties: the antiferromagnetic exchange coupling is reduced and finally disappears, the spin wave stiffness increases from 39.5 to 87.3 meVÅ^2 and Tc increases from 230 K to 478 K. We develop a simple model to quantify the competing interactions and to relate the antiferromagnetically coupled Fe moments to the Ni concentration. We find that the initial susceptibility increases with increasing Ni content along with a decrease of the temperature dependence.

I. INTRODUCTION

During recent years there has been a considerable interest in iron-rich rapid-quenched materials which, upon annealing, crystallize into a statε with ultrafine bcc-Fe grains. The high saturation magnetization of these materials, which approach that of standard bulk iron, is explained by the Fe atoms being organized in the same body-centered cubic (bcc) lattice as its conventional polycrystalline counterpart with only minor differences in lattice constant. The enhanced softness, i.e. the reduced effective magnetocrystalline anisotropy, is attributed to an averaging mechanism which is effective when the grain size is less than the width of a domain wall.

Numerous works about soft magnetic nanocrystalline materials have been published, especially about how functional properties depend on annealing conditions, but to our knowledge a clear understanding of how the structure and its magnetic properties gradually change upon heat-treatment is still lacking. We therefore find it appropriate to investigate in some detail the magnetic properties of as-quenched (as-Q) materials before annealing to a nanocrystalline state. We believe that a better understanding of the fundamental properties of the material before the crystallization will give useful clues of how to obtain optimum properties.

It is well known that the exchange interaction between two Fe atoms depends sensitively on the relation between their interatomic separation and the range of their 3d-orbitals. In an amorphous ferromagnet, antiferromagnetic exchange interaction may occur if the distribution of this relation between separation and 3d-range is broad. Indeed, disordered iron-rich materials often suffer from competing interactions, manifested by low T_C's and low saturation magnetization. Competing interaction is certainly detrimental from an application point of view and therefore it is motivated to study how this phenomenon may be suppressed. A previous study on a $Fe_{90-x}Zr_{10}Ni_x$ system (x=0,20) [1] shows that this Ni-substitution (20%) effectively removes the competing interaction and restores a ferromagnetic situation. However, no low-field data were provided nor were the observed changes fully quantified.

In this paper, we investigate and discuss the effect of replacing Fe with Ni in the $Fe_{91-x}Zr_7B_2Ni_x$ (x=0,5,10,15) alloy system. We develop a simple model allowing us to quantify the competing interactions and to relate them to the Ni concentration. We find that Ni replacement effectively decreases the amount of competing interaction accompanied with an increase in spin-wave stiffness constant, Tc, initial susceptibility and lower temperature dependence of the susceptibility.

II. EXPERIMENTAL

Ingots were prepared using conventional arc-melting in 99.999% Ar atmosphere. Rapid-quenched samples of nominal composition $Fe_{91-x}Zr_7B_2Ni_x$ (x=0,5,10,15) were prepared by the single-roll melt-spinning technique. The ribbons were approximately 20 μm thick and about 2 mm wide. DC magnetization measurements were carried out using a Quantum $MPMS_2$ SQUID magnetometer at temperatures ranging from 5 K to 300 K. The spectroscopic splitting factor, g was measured using ferromagnetic resonance (FMR). AC susceptibility measurements were performed using a home-built balanced mutual inductance bridge. We measure simultaneously both the elastic component, χ' and the viscous component, χ'' of the AC susceptibility at 190 Hz and in field-strengths varying from 5 mOe to 1 Oe depending on the particular situation. Curie temperatures for the samples with Tc's above the range accessible with the AC susceptometer were determined with a Perkin Elmer magneto-thermo gravimetric (TGS) instrument. All samples were checked for non-crystallinity with a Rigaku or Siemens 5000 X-ray diffractometer.

III. RESULTS AND DISCUSSION

A. High-Field Measurements

For brevity we label our samples Ni-0, Ni-5... letting the number denote the Ni concentration. In all experiments the Ni free sample singles out while the three other samples show a monotonic dependence with respect to the Ni concentration. In fig.1 we show the virgin M/H-curves at 5 K for samples of different composition.

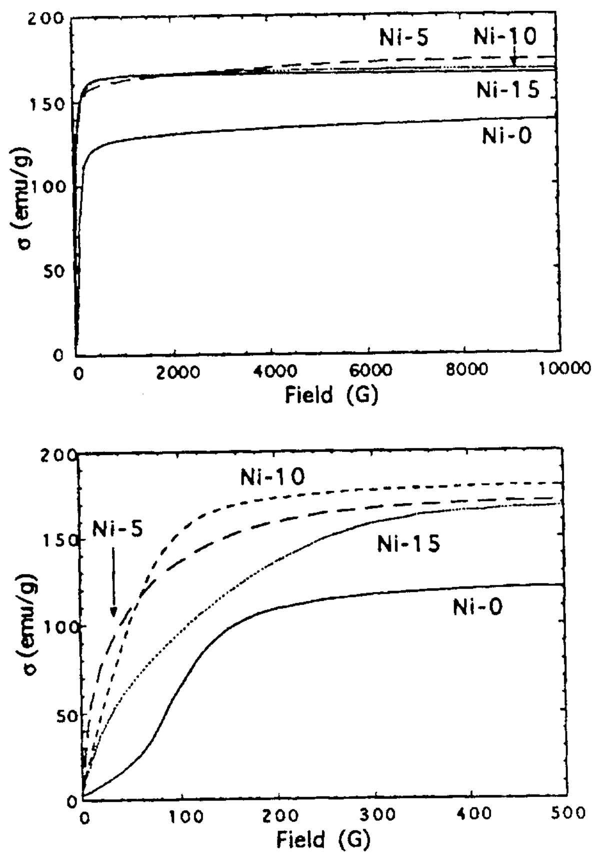

Fig.1 Virgin curves of the specific magnetization at 5 K as a function of applied field. Note the decrease in high-field susceptibility as the Ni concentration is increased. The lower graph shows the initial curves at lower fields.

Although the samples do not saturate completely we take the magnetization at 1 Tesla to be the saturation magnetization. With increasing Ni concentration the saturation magnetization is 131.1, 162.7, 174.7, 171.3 emu/g, respectively. The magnetization in fields ranging from 7 to 10 kG is well fitted by a linear dependence. To get an estimate of the antiferromagnetic (AFM) coupling and a means to compare between the samples we interpret this linear term as being proportional to the amount of AFM coupling. The result is shown in fig.2. It is found that the high field susceptibility decreases with increasing Ni concentration. The presence of Ni helps the sample to saturate. In other words: Ni suppresses the antiferromagnetical coupling between Fe atoms.

In order to explain the values of the saturation magnetization we develop a simple model for the AFM coupling. Due to a distribution in the argument of the Bethe-Slater curve (quota of the interatomic distance and the size of the 3d-orbital) some Fe atoms will couple antiferromagnetically. Assuming the Fe and Ni moments to have their bulk values (2.216 μ_B and 0.516 μ_B, respectively) we propose the following simple expression for the saturation magnetization:

$$M_S = N_{Fe}\mu_{Fe} + N_{Ni}\mu_{Ni} - 2N_{AFM}\mu_{Fe} \qquad (1)$$

where N is the number of atoms and in particular N_{AFM} is the number of antiferromagnetically coupled Fe atoms. With this simple model we can now estimate N_{AFM} and relate it to the high field susceptibility and the Ni concentration. The result is also shown in fig.2. The fraction of antiferromagnetically coupled Fe atoms is 16% in the Ni free sample and decreases to 0.2% in Ni-15. The correlation with the high field susceptibility is obvious. It seems that the Ni atoms has an effect on the exchange interaction between Fe atoms in such a way that ferromagnetic coupling is favored. At a Ni concentration of 15% the antiferromagnetism is completely suppressed and the sample behaves as a soft ferromagnet.

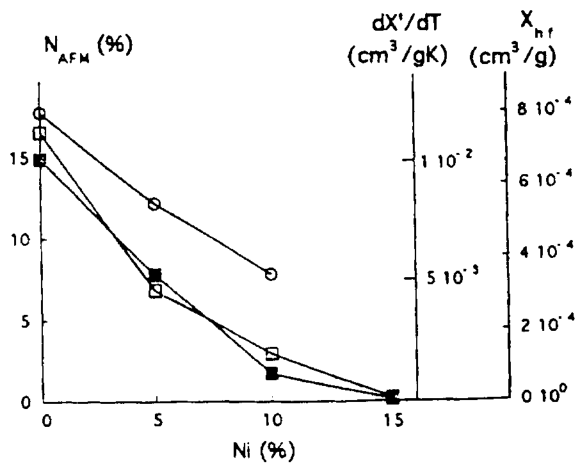

Fig.2 Fraction of antiferromagnetically coupled Fe atoms estimated with a simple model. The correlation with the high-field susceptibility is obvious. With 15% Ni the interaction between Fe atoms is purely ferromagnetic.

The Curie temperatures obtained by AC susceptibility or magneto-thermogravimetric measurements on these samples are 230 K, 335 K, 401 K and 478 K with increasing Ni concentration. Thus, it is seen that the addition of Ni increases T_c reflecting an increase in the mean exchange interaction.

Measurements of the temperature dependence of the saturation magnetization were also carried out. From the Bloch's law for the low lying spin wave excitations one expects a $T^{3/2}$ behaviour in the decrease of magnetization with increasing temperature. We use the expressions:

$$M_S(T) = M_S(0)\left[1 - BT^{3/2} - CT^{5/2}\right] \quad (2)$$

Our curves are well fitted with this temperature dependence and from the coefficients B and C we can calculate the stiffness constant D and the mean square range $\langle r^2 \rangle$ of the exchange interactions, through the relations:

$$B = \zeta(3/2)\left[g\mu_B / M_S(0)\right]\left[k_B / 4\pi D\right]^{3/2} \quad (3)$$

$$C = \zeta(5/2)\left[g\mu_B / M_S(0)\right]\left[k_B / 4\pi D\right]^{5/2}\langle r^2 \rangle \quad (4)$$

where ζ is the Riemann zeta function and g is the spectroscopic splitting factor. From FMR experiment g is estimated to 2.12, 2.08, 2.03, and 2.00 with increasing Ni concentration. The spectroscopic splitting factor represents the relative contribution of the orbital magnetic moment to the total magnetic moment. Our results indicate that the contribution of orbital magnetic moment decreases with increasing Ni concentration. From our analysis we obtain for the spin wave stiffness, D values of 39.7, 48.2, 62.8 and 87.3 meVÅ^2, and for the mean square range of exchange interaction 2.42, 3.21, 3.99 and 4.86 Å^2, with increasing Ni concentration. This result can be explained in terms of suppression of the antiferromagnetic coupling and an increase in the exchange interaction.

B. Low-Field Measurements

We have also measured the temperature-dependence of the AC susceptibility. As this kind of measurement is a probe of the magnetization process which in turn is sensitively affected by a number of phenomena of which we believe anisotropy and magnetoelasticity are the most important, we expect a more complex picture. In fig. 3 we show the elastic and viscous part of the susceptibility for the four different compositions. What we have found is that each sample has a threshold in the exciting field-strength above which the susceptibility is strongly fluctuating and field-dependant. The fluctuations weaken with lower field-strengths but despite using only 5 mOe for the Ni-15 sample we were not able to completely remove these complicating fluctuations. Therefore, the susceptibility curve for the Ni-15 sample should not be regarded with the same confidence as the other three.

However, referring to the reservation given in the previous section, there is a clear trend in the susceptibility data. By doing a linear fit of the temperature dependence of

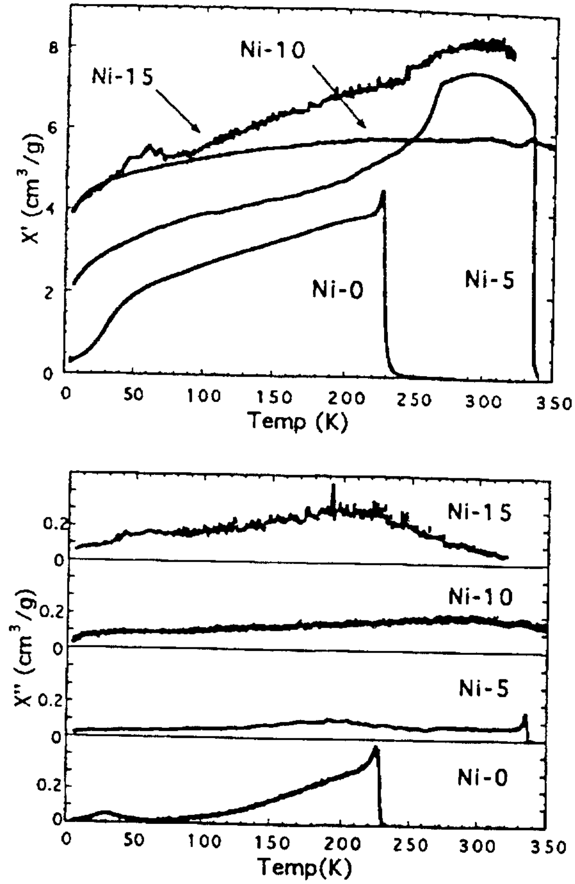

Fig.3 Ac susceptibility for all samples. Sample Ni-15 shows stronger fluctuations than the other samples despite the low exciting field (5 mOe). Frequency was 190 Hz and field-strength was 50 mOe rms except for the Ni-15 sample.

the elastic susceptibility over the temperature interval 80 - 200 K we can quantify this trend. The lower limit of this interval is motivated by the Ni-0 sample showing an additional phenomenon setting in at lower temperatures. The upper limit is restricted by T_c for the Ni-0 sample. The values of the temperature coefficient from this fit is shown if fig.2. We note a clear correlation between antiferromagnetic coupling and the temperature dependence of the susceptibility.

The extrapolated elastic susceptibility at zero temperature is shown in fig.4 together with T_c and D. From the plot we can see that this extrapolated zero-point elastic susceptibility to a large extent correlates with D and T_c which in turn is largely determined by the strength of the exchange interaction.

From both these observations concerning AC susceptibility, we are inclined to the conclusion that theaddition of Ni decreases the effective magnetic anisotropy and its temperature dependence.

Ni (%)	Tc (K)	M_S(5K) (emu/g)	D (meVÅ^2)	<r^2> (Å^2)	N_{APM} (%)
0	230	131.1	39.7	2.42	16.6
5	335	162.7	48.2	3.21	6.8
10	401	174.7	62.8	3.99	3.0
15	478	171.3	87.3	4.86	0.2

Table1 Curie temperature (Tc), saturation magnetization (emu/g), spin wave stiffness (D), mean square range of exchange interaction (<r2>) and fraction of antiferromagnetically coupled Fe atoms of glassy $Fe_{91-x}Zr_7B_2Ni_x$ alloys.

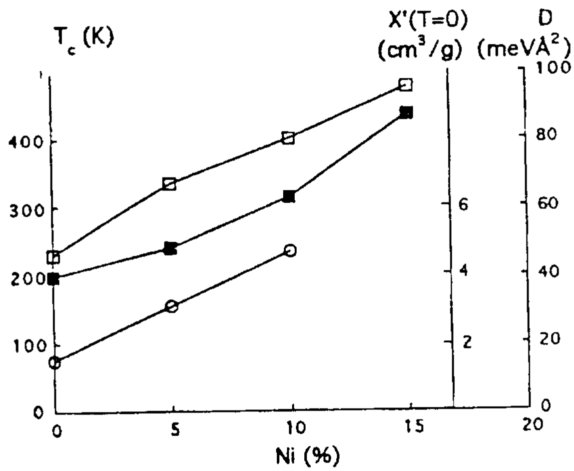

Fig.4 Graph showing the strong correlation between Tc, spin wave stiffness and zero-temperature AC susceptibility with increasing Ni content.

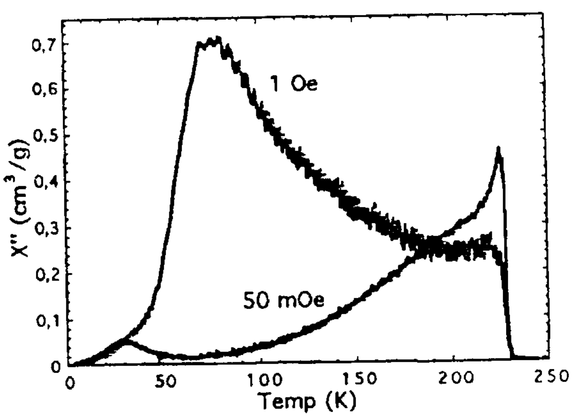

Fig.5 The viscous part (χ'') of the AC susceptibility for a $Fe_{91}Zr_7B_2$ sample (Ni-0) measured in two different driving fields, 50 mOe and 1 Oe. Note that the cusp at 30 K only is observable at the lower field-strength.

In ref.[2] a $Fe_{90}Zr_{10}$ system was investigated and the authors find that T_c = 235 K and a cusp at 23 K in the viscous part of the susceptibility when measured in a sufficiently low field (i.e. 0.1 Oe). They identify this cusp as the freezing temperature for a spin-glass, T_{sf}. In fig.5 we show the viscous part of the susceptibility of our $Fe_{91}Zr_7B_2$ (Ni-0) sample measured in 50 mOe and 1 Oe field. We note that our sample has a 5 K lower T_c and a corresponding 7 K higher T_{sf} = 30 K. Both these differences could be explained by a slightly higher coordination number for the iron atoms giving rise to higher degree of antiferromagnetic interaction. If this increased coordination number should be attributed to the slightly higher iron-concentration or to the replacement of Zr with the smaller B atoms or both is not clear at the moment.

IV. CONCLUSION

We have shown that the replacement of Fe with Ni in the glassy system $Fe_{91-x}Zr_7B_2Ni_x$ (x=0,5,10,15) effectively reduces the antiferromagnetic interaction and removes it completely at a Ni concentration of 15%.

The reduced antiferromagnetic interaction is manifested by an increase in T_c and stiffness constant and the low-field data show that the replacement also enhances the initial susceptibility and reduces its temperature dependence.

ACKNOWLEDGEMENT

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