A magnetocalorimetric study of spin fluctuations in amorphous Fe_xZr_{100-x}

A. LeR. Dawson and D. H. Ryan
Centre for the Physics of Materials Department of Physics, McGill University, 3600 University St., Montreal, Quebec, H3A 2T8, Canada

Low temperature calorimetry data on amorphous Fe_xZr_{100-x} samples near the ferromagnetic/paramagnetic phase boundary at $x=37.5$ are reported, as well as some magnetocalorimetry data in magnetic fields of up to 5 T. The data are analyzed in terms of two models, one describing the effect of spin fluctuations (SF) and the other the effect of superparamagnetic clusters. The data are shown to favor the SF model and taken with earlier resistivity work, provides convincing evidence for the existence of SF in a-Fe_xZr_{100-x}.

Spin fluctuations (SF) are nonmonodispersive long wavelength magnetic excitations of characteristic energy T_{SF}, not accounted for by mean-field theories, which were predicted to apply to nearly ferromagnetic Fermi liquids and explained the specific heat capacity (C_P) of liquid ^{3}He.[1] Ikeda *et al.*[2] have given an extensive review of the quenching by high (~10 T) magnetic fields of the SF contribution to the low-temperature C_P. Their study surveyed several highly exchange-enhanced d- and f-band magnets for which the Stoner enhancement factor, S, is greater than 10. $Ni_{3+x}Al_{1-x}$, for example, exhibits a transition from an exchange-enhanced paramagnet to a weak ferromagnet for small values of x. SF models have been shown to be necessary to explain the values of both the Curie temperature and the ordered moment in Ni_3Al.[3] A recent magnetocalorimetry study of $Ni_{3+x}Al_{1-x}$[4,5] used elastic constant measurements to separate the phonon contribution to C_P and detected a small SF enhancement, which was greatest at the critical composition. Field quenching of this enhancement was found to be in agreement with predictions from T_{SF} measured in zero field. The effect of a magnetic field also ruled out the presence of superparamagnetic clusters due to possible compositional inhomogeneities in their samples, which could also have accounted for the zero-field data.

Amorphous d-band metals offer many advantages for the study of SF. The rapid quenching from the liquid state leads to a high degree of compositional homogeneity and inhibits magnetic cluster formation. Furthermore, slightly varying the sample composition should not significantly change the phonon C_P, a complication which can occur in crystalline systems. a-Fe_xZr_{100-x} is an ideal candidate system for the study of SF. It is a good glass former[6] in the range $20<x<43$, where it exhibits three distinct phases, superconductivity for $x<30$, ferromagnetism for $x>37.5$ and paramagnetism for intermediate compositions. The susceptibility of the paramagnetic alloys suggests that they are strongly exchange-enhanced paramagnets with Stoner factors approaching 10, and the superconducting alloys exhibit a mass enhancement factor possibly arising from SF.[7] A low-temperature resistivity study of alloys near $x=37.5$ showed a strong temperature dependence which could be analyzed using a model including scattering by SF.[8] This analysis yielded rough estimates for T_{SF} which were as low as 20 K.

Previous C_P studies of a-Fe_xZr_{100-x} at broadly spaced compositions have been discussed in terms of a cluster model.[9,10] In this preliminary work, we report on the low-temperature C_P of several closely spaced a-Fe_xZr_{100-x} alloys near the ferromagnetic phase boundary at $x=37.5$. We have analyzed our data in terms of both a magnetic cluster model and a SF-model.

Appropriate amounts of Fe (99.98%) and Zr (99.9%) were induction melted on a water-cooled copper boat in a Ti-gettered argon atmosphere. The boules were twice remelted to ensure homogeneity. The alloys were then rapidly quenched by melt spinning in a He atmosphere with a tangential wheel speed of around 50 m/s, yielding meter length ribbons 1 mm wide and ~20 μm thick. Cu K_α x-ray diffraction using an automated Nicolet–Stoe powder diffractometer showed the samples to be amorphous. Some samples near $x=30\%$ showed small crystal peaks which did not appear on the wheel side of the ribbon and could be easily removed from the free side by a very light sanding. Sample compositions were determined by electron microprobe analysis.

Absolute C_P data were measured between 2 and 25 K using a time relaxation technique[11] modified by the use of an ac chopped[12] Au-0.07% Fe thermocouple and a thick film ruthenium oxide resistance thermometer.[13] The microcalorimeter was checked for accuracy by measuring gold and copper standards[14] and the overall accuracy and precision were each found to be 2%. Approximately 40 mg of ribbon were wound into a ~7-mm-diam coil and silver pasted to the addenda. This mounting technique allows large sample loading with a fast internal relaxation time. The calorimeter could be placed in the bore of a 5 T superconducting solenoid with the field axis parallel to that of the sample coil to minimize demagnetization effects. The small magnetoresistance of the carbon glass thermometer was corrected for using a field-independent capacitance thermometer.

Figure 1 shows the specific heat of several of our a-Fe_xZr_{100-x} samples. Normally, for $T<\Theta_D/40$, C_P can be written as

$$C_P=\gamma T+\beta T^3, \tag{1}$$

where

$$\gamma=\tfrac{1}{3}\pi^2k_B^2(1+\lambda_{e-p})N_0(E_F)\equiv(1+\lambda_{e-p})\gamma_0$$

and

$$\beta=\frac{(1.944\times10^6\ \text{mJ/mol K})}{\Theta_D^3}.$$

0021-8979/94/75(10)/6837/3/$6.00

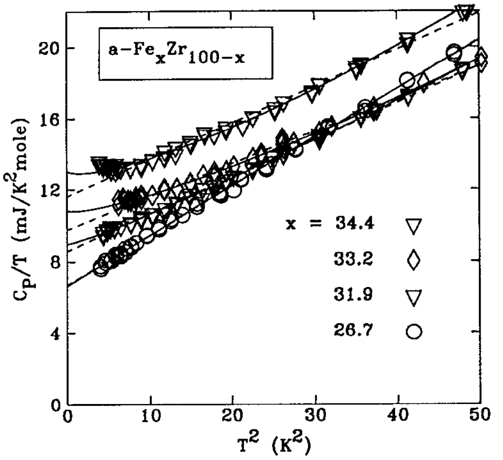

FIG. 1. C_P/T vs T^2 for a-Fe$_x$Zr$_{100-x}$. The dashed and solid lines are fits to Eqs. (1) and (3), respectively.

Since $\Theta_D \sim 200$ K,[9] we expect plots of C_P/T vs T^2 to yield straight lines. This is clearly not the case, as Fig. 1 shows definite upturns for some alloys below $T^2 = 10$ K^2.

In the presence of SF, Eq. (1) becomes[4]

$$C_P = \gamma_0 T\left(\frac{m^*}{m}\right) + \beta T^3 + D T^3 \ln\left(\frac{T}{T_{\mathrm{SF}}}\right). \tag{2}$$

This may be more conveniently rewritten as

$$C_P = AT + BT^3 + DT^3 \ln T, \tag{3}$$

where

$$B = \beta - D \ln T_{\mathrm{SF}}$$

and

$$A = \gamma_0 m^*/m = \gamma_0(1 + \lambda_{e-p} + \lambda_{\mathrm{spin}}),$$

λ_{spin} is the the SF electron mass enhancement.

The theory also predicts that both A and D increase with the Stoner factor S. This is not surprising since a large electronic specific heat γ and the existence of magnetic order in itinerant systems are both associated with a high density of states at the Fermi level. Plotted as C_P/T vs T^2, Eq. (2) shows a characteristic upturn at temperatures below T_{SF}. Since Eq. (2) is only valid for $T \ll T_{\mathrm{SF}}$, in fitting to it, the range of data must be restricted to temperatures not too far above the upturn.

The parameters derived from fits of Eq. (3) to the data in Fig. 1 are shown as a function of iron content in Fig. 2. The composition dependences of the coefficients of the linear term, A, and the $T^3 \ln T$ term, D, are very similar as expected from their dependence on S. We take this similarity as support for the SF model. Assuming $\lambda_{\mathrm{spin}} = 0$ for a-Fe$_{26.7}$Zr$_{73.3}$, and using $\lambda_{e-p} = 0.4$[9] we can calculate γ_0 for $x = 26.7$. Assuming γ_0 and λ_{e-p} remain unchanged for $x = 34.4$, we obtain $\lambda_{\mathrm{spin}} = 1.4$ for a-Fe$_{34.4}$Zr$_{65.6}$.

We have also fitted Eq. (1) to the data between 7 and 10 K, where the SF term is expected to be small. The β resulting from these fits is shown in Fig. 3. Analysis of the a-Fe$_{26.7}$Zr$_{73.3}$ data, which exhibits normal metallic behavior at low temperatures, shows that the specific heat drops below that predicted by a Debye function even below 7 K. Therefore, we cannot exactly determine the phonon contribution to B in Eq. (3) by extrapolation from the high-temperature fits. The departure from T^3 behavior appears as a slight downturn in a C_P/T vs T^2 plot and leads us to underestimate D, and results in slightly negative values in some cases.

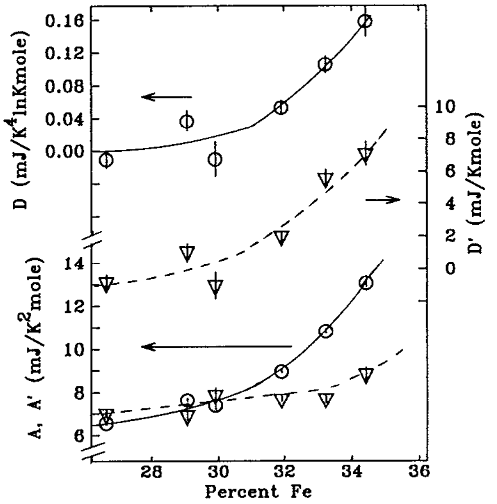

FIG. 2. Some of the parameters resulting from fits of the C_P data below 7 K: (○) A and D from Eq. (3) and (▽) A' and D' from Eq. (4). The solid and dashed lines are guides for the fits to Eqs. (3) and (4), respectively. Error bars are also calculated by the fitting program.

Nonetheless, using the high-temperature β value and the definition of B in Eq. (3) we estimate T_{SF} for our samples which show a clear deviation from normal behavior [Eq. (1)]. These are shown in Fig. 3 together with the approximate curve obtained from the resistivity of a-Fe$_x$Zr$_{100-x}$.[8] Altounian *et al.*[15] have done a more detailed determination of T_{SF} through a study of the isostructural system

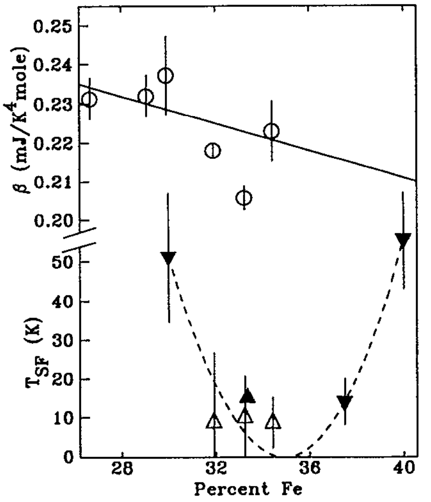

FIG. 3. (○) Phonon C_P coefficient, β, resulting from fits of the data between 7 and 10 K to Eq. (1). The straight solid line is a guide to the eye. Displayed in the lower section are approximate values of T_{SF} whose derivation is discussed in the text (△). Data taken from resistivity studies of Ref. 8 (▼ and dashed line) and Ref. 15 (▲) are also shown for comparison.

a-$(\mathrm{Fe}_y\mathrm{Ni}_{100-y})_{33.3}\mathrm{Zr}_{66.7}$. Substitution of Fe by Ni allowed separation of the resistivity due to SF from that due to electron–phonon scattering since for $y<0.4$, the latter process dominates. They find $T_{\mathrm{SF}}=15$ K for $y=100$ which is also shown in Fig. 3. We take the good agreement between the T_{SF} derived from two very different measurements as further support for the SF model. The values of T_{SF} and that of λ_{spin} discussed earlier are similar to those for $\mathrm{Ni}_{3+x}\mathrm{Al}_{1-x}$ and so a-$\mathrm{Fe}_x\mathrm{Zr}_{100-x}$ can probably be classed as the same type of spin fluctuator.[2]

We now turn our attention to the only other plausible explanation for the data. Upturns similar to those of Fig. 1 have been seen the C_P of $\mathrm{Cu}_{60}\mathrm{Ni}_{40}\mathrm{Fe}_{0.02}$[16] and result from superparamagnetic moment clusters which form about the Fe atoms and extend for several lattice spacings. The clusters contribute an extra component to C_P as they are small enough that their energy in the local crystal field is comparable with k_BT. This contribution to C_P can be described as a Schottky-like function which we have approximated by a constant to yield the expression:

$$C_P=A'T+\beta'T^3+D'. \tag{4}$$

The fits are as good as those to Eq. (3) and the results are also shown in Fig. 2. The size and composition dependence of the D' term resembles that of and earlier study[10] however we do not observe a divergence in Θ_D. Identifying D' with k_B times the number of magnetic clusters per mole, we can derive a lower bound of order 10^{-3} clusters per mole. Such a small number of clusters seems unlikely in the presence of so much iron. While SF and magnetic clusters both yield an enhanced susceptibility, a more complete study of the high-field magnetization could rule out the magnetic cluster picture.

Finally, we discuss the magnetocalorimetry results. In a sample with magnetic clusters, the applied field adds to the local field felt by the clusters so that when the two are of the same order, the magnetic C_P component, D', should increase significantly since we are on the high-temperature side of the Schottky anomoly.[16] These local fields must be less than 1 T, since we know that the Schottky peak is at $T\leqslant 1\ \mathrm{K}\sim\mu_B\times(1\ \mathrm{T})$, so that we would expect a significant change in the magnetic C_P at 5 T. For SF, the effect of a magnetic field appears as a change in the linear C_P:[2]

$$\frac{\gamma(B=0)-\gamma(B)}{\gamma(B=0)}=0.1\,\frac{S}{\ln S}\left(\frac{\mu_B B}{k_B T_{\mathrm{SF}}}\right)^2. \tag{5}$$

With $T_{\mathrm{SF}}=10$ K and $S=10$, we would expect a decrease in γ of order 3% in a field of 5 T. The C_P of $x=31.6$ and $x=30.3$ samples were measured in fields of 0, 3.5, and 5 T. No change was found to within 3%. Our results, therefore, support the SF picture.

In conclusion, we have presented observations of a spin fluctuation contribution to C_P in a nearly ferromagnetic amorphous alloy. While fits to the data cannot unequivocally distinguish between a SF model and a magnetic cluster model, interpretation of the fit parameters favors the SF model, as does the preliminary field work. Taken together with earlier results on the low-temperature resistivity[8,15] and susceptibility,[7] this is strong evidence of spin fluctuations in this system.

This work was supported by grants from the Graduate Faculty of McGill University, the Walter C. Sumner Foundation, Nova Scotia, the Natural Sciences and Engineering Research Council of Canada and Fonds pour la formation de chercheurs et l'aide à la recherche, Québec.

[1] S. Doniach and S. Engelsberg, Phys. Rev. Lett. **17**, 750 (1966).

[2] K. Ikeda, S. K. Dhar, M. Yoshizawa, and K. A. Gscheidner, Jr., J. Magn. Magn. Mater. **100**, 292 (1991).

[3] G. G. Lonzarich and L. Taillefer, J. Phys. C **18**, 1 (1985).

[4] S. K. Dhar and K. A. Gschneider, Jr., Phys. Rev. B **39**, 7453 (1989).

[5] S. K. Dhar, K. A. Gschneider, Jr., L. L. Miller, and D. C. Johnston, Phys. Rev. B **40**, 11 488 (1989).

[6] Z. Altounian, T. Guo-hua, and J. O. Ström-Olsen, J. Appl. Phys. **57**, 1777 (1985).

[7] E. Batalla, Z. Altounian, and J. O. Ström-Olsen, Phys. Rev. B **31**, 577 (1985).

[8] J. Ström-Olsen, Z. Altounian, R. W. Cochrane, and A. B. Kaiser, Phys. Rev. B **31**, 6116 (1985).

[9] D. G. Onn, L. Q. Wang, Y. Obi, and K. Fukamichi, J. Non-Cryst. Solids **61**, 1149 (1984).

[10] M. Matsuura, U. Mizutani, and K. Fukamichi, in *Proceedings of the Fifth International Conference on Rapidly Quenched Metals*, edited by S. Steeb and H. Warlimont (North-Holland, Amsterdam), Vol. 1, p. 1019.

[11] R. Bachman, F. J. diSalvo, T. M. Geballe, R. L. Greene, R. E. Howard, C. N. King, M. C. Kisch, K. N. Lee, R. E. Schwall, H. U. Thomas, and R. B. Zubeck, Rev. Sci. Instrum. **43**, 205 (1972).

[12] J. R. Anderson and D. R. Zrudsky, Rev. Sci. Instrum. **44**, 316 (1971).

[13] Q. Li, C. H. Watson, R. G. Goodrich, D. G. Haase, and H. Lukefahr, Cryogenics **26**, 467 (1986).

[14] D. L. Martin, Can. J. Phys. **65**, 1104 (1987).

[15] Z. Altounian, S. Dantu, and M. Dikeakos (unpublished).

[16] R. L. Falge, Jr. and N. M. Wolcott, J. Low Temp. Phys. **5**, 617 (1971).