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Specific Heat of the Dilute Antiferromagnetic System Fe$_x$Zn$_{1-x}$F$_2$

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Abstract. The specific heat ($c_p$) of the dilute antiferromagnet Fe$_x$Zn$_{1-x}$F$_2$ has been measured in absence of external magnetic fields for $x = 0, 0.26, 0.31, 0.34, 0.36, 0.38, 0.41, 0.45, 0.56, 0.88, 0.97, and 1.0$. For $x > 0.45$, a sharp peak associated to the antiferromagnetic (AF) phase transition at $T_N(x)$ is the only observed feature. For $0.31 \leq x \leq 0.41$, this peak becomes smaller with decreasing $x$ and a rounded bump appears at higher temperatures $T$. Closer to the percolation concentration ($x_p = 0.24$), the peak characteristic of the AF phase transition disappears and the rounded bump becomes the only observed feature. The low-$T$ behavior confirms a crossover from AF long range order at large $x$ to a spin glass behavior close to $x_p$. At intermediate $x$, the low-$T$ joint signature of both phenomena indicates a coexistence of AF order and a cluster-glass phase. The $x$-dependence of the Néel temperature was accounted for using a simple phenomenological model.

1. Introduction
Specific heat studies of pure FeF$_2$ and of its isomorph compound ZnF$_2$ began long way ago [1]. In their seminal work, Stout and Catalano found that FeF$_2$ becomes antiferromagnetic (AF) below 78.3 K while ZnF$_2$ was found to be diamagnetic. Nearly a decade later (1966), Wertheim et al. performed the first magnetic studies in dilute Fe$_x$Zn$_{1-x}$F$_2$ using Mossbauer effect at zero applied magnetic field [2]. Taking the advantage that FeF$_2$ and ZnF$_2$ have the same structure and that their lattice parameters are nearly the same, they investigated crushed powders obtained from polycrystalline samples from rapidly quenching the melt of a proper composition of FeF$_2$ and ZnF$_2$. Using the onset of the AF order they established the dependence of the Néel temperature of Fe$_x$Zn$_{1-x}$F$_2$ to be proportional to $x$ ($T_N(x)=xT_N(x=1)$) for $x$ in the range 0.25-1.0. Unfortunately, this work was not conclusive whether the criterion used to define $T_N(x)$ corresponded indeed to the establishment of long range order or to short range order (SRO) as seen in AF clusters. One decade later (1974), Ahlers et al. used the heat capacity to determine the critical exponents and the amplitude ratio associated to the AF phase transition in FeF$_2$ [3]. Few years later (1978), Tahir-Kheli and McGurn used coherent-potential and random-phase approximations to calculate $T_N(x)$ in an attempt to account for the results reported by Wertheim et al. [4]. Their analysis concluded by demanding for more precise $T_N(x)$ data and more experimental results. This would allow one to test if the assumption made by them, namely that the exchange parameters are independent of the zinc concentration, was a good one. However, it was in the context of the random-field Ising model (RFIM) problem aroused that experimental and theoretical studies in the dilute-AF Fe$_x$Zn$_{1-x}$F$_2$ increased substantially. Local random fields couples linearly to the antiferromagnetic order

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parameter producing significant changes in the magnetic properties and in its critical behavior. An Ising spin-glass phase dominate the whole phase diagram for \( x \) close to \( x_p \) (\( = 0.24 \)) [5-14].

Despite the large number of experimental results reported for the dilute-AF \( \text{Fe}_{x}\text{Zn}_{1-x}\text{F}_2 \) there are very few on heat capacity in zero field. This is even more critical for samples with \( x \) near \( x_p \). Moreover, some of the data were obtained by applying magnetic field or for thick samples where concentration gradient are present. In this paper we report heat capacity data for a large range of sample concentration in \( \text{Fe}_{x}\text{Zn}_{1-x}\text{F}_2 \) at zero magnetic field from room temperature down to 1.8 K.

![Figure 1. \( c_p \) vs. \( T \) data for \( x = 0.88 \). The upper and lower insets are \( c_p \) for \( \text{ZnF}_2 \) and low-\( T \) \( c_{\text{mag}} \), respectively.](image1)

![Figure 2. \( c_p \) vs. \( T \) data for \( x = 0.36 \). The inset shows the low-\( T \) \( c_{\text{mag}} \) data.](image2)

### 2. Samples and Results

The insulating rutile-tetragonal compound \( \text{FeF}_2 \) (\( \text{ZnF}_2 \)) has lattice parameters \( a_0 = 0.3304 \) (0.3134) nm and \( c_0 = 0.4697 \) (0.4703) nm [4]. Besides the similarity in the lattice parameters of these compounds, a large uniaxial single-ion crystal-field anisotropy oriented along the \( c_0 \) axis (\( D \) is equal to 6.5 cm\(^{-1}\) for \( \text{FeF}_2 \) and 7.3 cm\(^{-1}\) for \( \text{ZnF}_2 \)) lead to the ability to substitute Fe- by Zn-ions and grow dilute samples of the antiferromagnetic system \( \text{Fe}_{x}\text{Zn}_{1-x}\text{F}_2 \). Rods of crystalline \( \text{Fe}_{x}\text{Zn}_{1-x}\text{F}_2 \) were prepared by a Czochralski technique where the iron and zinc evaporation was reduced by slightly pressurizing the melt. In order to minimize concentration gradient we have scanned all samples with a laser beam and used a birefringence technique to select a slice of the boule in positions with smaller variation of the birefringence amplitude. The iron concentrations of the samples used in the present work were determined from density measurements considering the Vegard’s law which empirically stipulates a linear relation between crystal lattice constant and \( x \). The accuracy of this method is better than 0.1%.

For the present work we used samples with concentrations \( x = 0, 0.26, 0.31, 0.34, 0.36, 0.38, 0.41, 0.45, 0.56, 0.88, 0.97, \) and \( 1 \). The heat capacity measurement were done in near squared thin slabs with dimensions close to 4.0x4.0x1.0 mm\(^3\) using a microcalorimeter (PPMS-Quantum Design) for \( 1.8 \leq T \leq 300 \) K and at zero applied field. In this kind of system, \( c_p \) is measured using a thermal relaxation technique [15]. The magnetic contribution to \( c_p \) (\( c_{\text{mag}} \)) was determined for each sample by subtracting from \( c_p \) the heat capacity of a \( \text{ZnF}_2 \) sample.

The closed circles in figure 1 shows a typical \( c_p \) versus \( T \) data for a sample with \( x > 0.5 \). The upper inset shows the \( c_p \) data for \( \text{ZnF}_2 \) while the lower one shows the \( c_{\text{mag}} \) data close to \( T_N(x) \). It is clearly
seen from $c_{\text{mag}}$ that the $T$-dependence is mainly determined by the logarithmic divergence (peak) in $c_p$ at the Néel temperature which is associated to the establishment of long range order (LRO). Besides the LRO peak a bump is also seen in $c_{\text{mag}}$ for samples with $x < 0.41$ (see figure 2). Such a bump is very similar to those found in cluster-glass systems or in magnetic systems presenting SRO. A set of low-$T$ $c_{\text{mag}}$ data is shown in figure 3 for all measured samples. One can see how the system evolves from pure FeF$_2$ up to close $x_p$. For instance, one sees that the LRO peak shifts to lower $T$ and its amplitude diminishes with decreasing $x$. Now, plotting the Néel temperature as a function of $x$ one determines a phase diagram as shown in figure 4. Also shown are some values of $T_N(x)$ measured by different techniques [6-14], the temperature corresponding to the maximum in the bumps ($T_{\text{bump}}$), the mean-field result (broken-line) and a fit (solid line) of a phenomenological model discussed below.

![Figure 3](image-url)  
Figure 3. Low-$T$ $c_{\text{mag}}$ data for all measured samples. Note that a bump appears for $x < 0.4$.

![Figure 4](image-url)  
Figure 4. Phase diagram determined by $T_N(x)$.

The glassy phase is represented by $T_{\text{bump}}$. The solid line is a fit to a model (see text).

3. A phenomenological model

It has been widely accepted that $T_N(x)$ is proportional to $x$ for high concentrations [16]. However, as shown in figure 4, a strong deviation from this linear behavior is seen for low values of $x$. This probably results from the fact that it is more difficult to establish LRO in samples with higher dilution in which SRO becomes dominant. Moreover, if effects such as variations in the exchange interactions due to the dilution are not considered, the number of magnetic nearest neighbors $z$ (= 8 for pure FeF$_2$) should play a most important role in determining $T_N(x)$, e.g., $T_N(x) \propto z$. Assuming that this is the case here, we can apply the binomial distribution $Pr(k,n,p) = \{n!/k!(n-k)\} \ p^k \ (1-p)^{n-k}$ to write down the probability $P(x)$ of finding magnetic ions close to each other in a diluted system. $k$ is the success rate of making $n$ trials of events with a probability $p$ to occur. For the present case, $x$ is the probability, $k = 1$ and $n = 1, 2, 3, \ldots$ In other words, we like to succeed well at least once ($k = 1$) when we visit the lattice $n$ times trying to find a magnetic ion with probability $x$ of be found. The need of $T_N(x) \geq 0$ only for $x \geq x_p$ it is taken into consideration in our model by replacing $x$ by $x-x_p$. This is enough to insure that $P(x_p) = 0$. Using this assumption and considering the $n = 1$ and 2 terms of $Pr(k,n,p)$, it can be shown that:

$$P(x) \approx a(x-x_p) + 2b(x-x_p)(1-x).$$  (1)
Now, we use $P(x)=1$ to find $a = 1/(1-x_p)$. Thus we have,

$$T_A(x)/T_A(x=1) = (x-x_p)/(1-x_p) + 2b(x-x_p)(1-x),$$

(2)

where the only one undetermined parameter is $b$ since both $T_A(x)$ and $x_p$ can be measured. A fitting of equation 2 to the experimental data $T_A(x)/T_A(x=1)$ (solid line in figure 4) yields $b = 0.459$. By including higher order terms will introduce more fitting parameters with little improving in the fit.

4. Discussion and conclusions

A difficulty that has been present in dilute-AF systems, like Fe$_{1-x}$Zn$_x$F$_2$, is the need to establish some consistent criterion to define $T_A(x)$ at intermediate values of $x$ when a cluster-glass phase coexist with AF LRO. Furthermore, it is well known that AF short range order starts well before the long range order is completed. These difficulties lead to some authors to take the linear dependence in $x$ as being correct even close to $x_p$. Specific heat measurements, on the other hand, is a very good tool to determine $T_A(x)$. $c_p$ is sensitive to the degrees of freedom and can distinguish the short range magnetic order from a phase transition. Indeed, as shown in figures 2 and 3, for low $x$ a bump which remains even close to $x_p$ was observed for $T$ above the temperature corresponding to the peak associated to the AF LRO order, which disappears at $x_p$. When the temperature is reduced SRO takes place forming AF clusters. By reducing the thermal energy further the LRO is established between the cluster if there are enough magnetic ions to guarantee that the magnetic interactions percolates along the sample ($x > x_p$).

This scenario is consistent with the proposed phenomenological model which took into consideration the non-uniformity in the atomic distribution of the magnetic ions.

In summary, we carried out $c_p$ measurements in thin slabs of Fe$_{1-x}$Zn$_x$F$_2$ samples. The values of $x$ investigated fulfilled a range where there was no available data. Moreover, it was found that for high values of $x$ a peak associated to the AF-LRO is the most pronounced feature in the $T$-dependence of $c_p$. For low $x$, however, a bumps characteristic of SRO appears at temperatures well above $T_A(x)$. The proposed model was found to fit nicely the $T_A(x)$ data reported in the present work as well as other experimental data obtained by using techniques other than specific heat.

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