Magnetic Properties of Zr_9Ni_{11} Intermetallic Compound

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We report on a very interesting magnetic behavior in the intermetallic compound Zr_9Ni_{11}, namely, (i) spin-glass behavior and (ii) fluctuations in the magnetization versus temperature curves. The magnetic properties are consistent with structural results obtained by neutron diffraction and by scanning and transmission electron microscopies. The fluctuations are believed to arise from the Dzyaloshinskii-Moriya interactions occurring in the Zr_9Ni_{11} compound. Between 7.86 kA/m and 31.85 kA/m, the temperature (Tp) of the zero-field cooled (M_{ZFC}) peak shifted to lower temperatures with increasing field. Tp is found to be proportional to H^b, where H is the applied field and the exponent $b < 1$. The value of b is found to be 0.68, which is close to the de Almeida-Thouless $2/3$ power law that applies to spin glasses. Published neutron diffraction data showed that a Zr_9Ni_{11} compound possessed Zr_9Pt_{11}-type tetragonal structure with columnar atomic chains parallel to the c axis and consisting of alternating Zr and Ni atoms. Small fluctuations present in the M_{FC} versus T plot at 31.85 kA/m are believed to be the result of atomic displacements along these chains over short distances. Another interesting featured observed in the Zr_9Ni_{11} compound is the fact that at 3.98 kA/m the M_{ZFC} values reside mostly above the corresponding M_{FC} values.

***Index Terms*—Dzyaloshinskii-Moriya interactions, spin glass, ZFC and FC plots.**

I. Introduction

As PART OF a study on the (transition metal)$_9$-(transition metal)$_{11}$ intermetallic compounds, we carried out some exploratory magnetic measurements. Unexpectedly, in one of these compounds (Zr_9Ni_{11}), we observed an unusual magnetic behavior: (i) spin-glass behavior that had not been previously seen in this 9–11 family of compounds, and (ii) fluctuations in the magnetization versus temperature curves. Here we report on the magnetic measurements that were carried out on the Zr_9Ni_{11} intermetallic compound. Though the main focus of the present study is on the magnetic property measurements, we shall also make brief reference to a parallel crystal structure study conducted on the same Zr_9Ni_{11} compound and whose results have been recently published [1].

II. Experimental Procedure

The sample of nominal composition Zr_9Ni_{11} was prepared by arc-melting at the alloy melting facility of the American Dental Association at NIST, using a water-cooled copper hearth in an argon atmosphere under ambient pressure starting with the appropriate ratio of the component elements. The purity of the starting constituents was 99.9% mass fraction. After arc melting, the sample was homogenized in vacuum at 1030°C for one week, and then water quenched. The magnetic properties of the homogenized sample were characterized by SQUID magnetometry, while its crystal structure, microstructure, and chemistry were examined by powder neutron diffraction, by transmission and scanning electron microcopies (SEM), and by energy dispersive spectroscopy (EDS).

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III. Results and Discussion

Fig. 1(a) and (b) show the temperature dependence of the zero-field-cooled magnetization (M_{ZFC}) and the field-cooled magnetization (M_{FC}) curves of the Zr_9Ni_{11} compound in a dc field of 3.98 kA/m (top panel) and of 7.96 kA/m (bottom panel), respectively. The M_{ZFC} at 3.98 kA/m shows a peak centered at about 20 K, whereas the M_{ZFC} at 7.96 kA/m shows a peak centered at 36 K; the corresponding M_{FC} curves at both field values show an upturn at low temperatures. The M_{ZFC} and M_{FC} curves for dc field values of 23.90 kA/m and 31.85 kA/m are presented in Fig. 2(a) and (b), respectively. In this latter set of curves, the M_{ZFC} peak for the lower field value is centered at 18 K (top panel), whereas for the higher field it is centered at 15 K (bottom panel). From the comparison of the results shown in Figs. 1(b) and 2(a) and (b) it can be concluded that from 7.96 kA/m to 31.85 kA/m the dependence of the magnetization with temperature of both the M_{ZFC} and M_{FC} plots display a similar trend, except that the M_{ZFC} peak temperature (T_p) shifts to lower temperatures with increasing field. On the other hand, as it can be observed from the plots shown in Fig. 3, there is no discernible difference between the M_{ZFC} and M_{FC} at 39.80 kA/m; in fact, the two plots are essentially superimposed on each other. Though not shown, the M_{ZFC} and M_{FC} plots for field values higher than 39.80 kA/m are similar to the 39.80 kA/m plots. That is, the corresponding M_{ZFC} and M_{FC} plots are superimposed on each other they are essentially identical.

However, the trends of the M_{ZFC} and M_{FC} versus T plots for field values in the range of 0.16 kA/m to 7.96 kA/m are somewhat different than those in the 7.96 kA/m to 31.85 kA/m range. In fact, as shown by the M_{ZFC} peak temperature (T_p) versus applied field plot presented in Fig. 4, in the 0.16 kA/m to 7.96 kA/m field range, T_p increases with increasing field, whereas the M_{ZFC} segment is quite smooth. A possible mechanism to explain the presence of these fluctuations in the M_{FC} versus T curve at this field value is given below.

The fluctuations of varying amplitudes (small peaks) present in the M_{FC} versus T plot at 31.85 kA/m are believed to arise

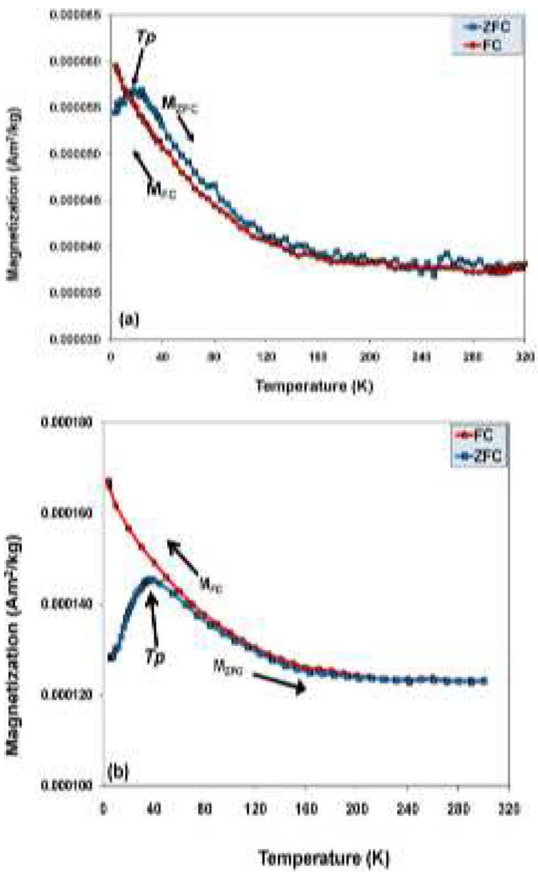


Fig. 1. (a). $\mathrm{M_{ZFC}}$ (circles) and $\mathrm{M_{FC}}$ (squares) versus T plots at 3.98 kA/m. (b) $\mathrm{M_{ZFC}}$ (circles) and $\mathrm{M_{FC}}$ (squares) versus T plots at 7.96 kA/m.

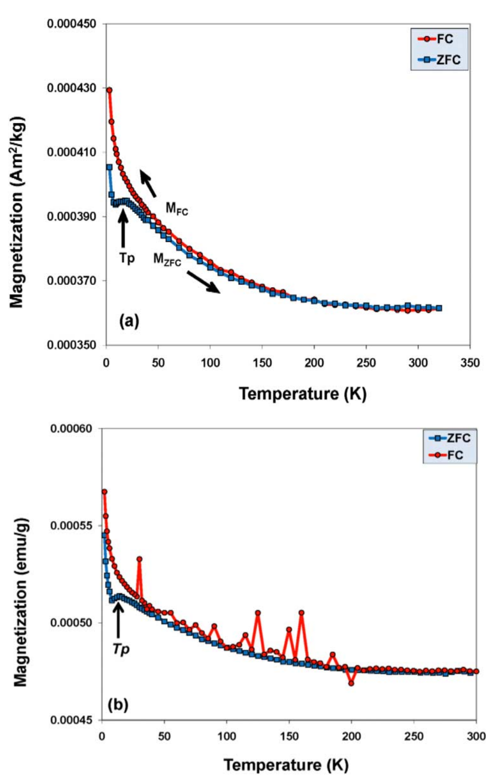


Fig. 2. (a) $\mathrm{M_{ZFC}}$ (circles) and $\mathrm{M_{FC}}$ (squares) versus T plots at 23.90 kA/m. (b) $\mathrm{M_{ZFC}}$ (circles) and $\mathrm{M_{FC}}$ (squares) versus T plots at 31.85 kA/m.

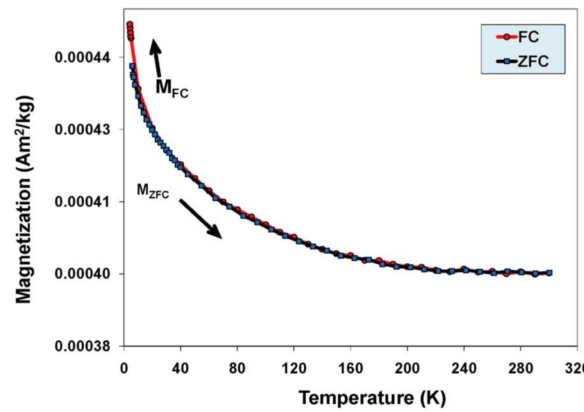


Fig. 3. $\mathrm{M_{ZFC}}$ (open circles) and $\mathrm{M_{FC}}$ (solid circles) versus T plots at 39.81 kA/m.

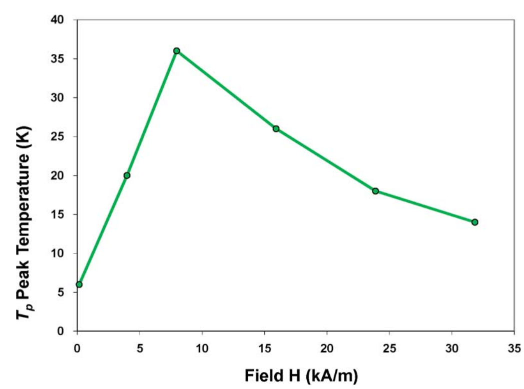
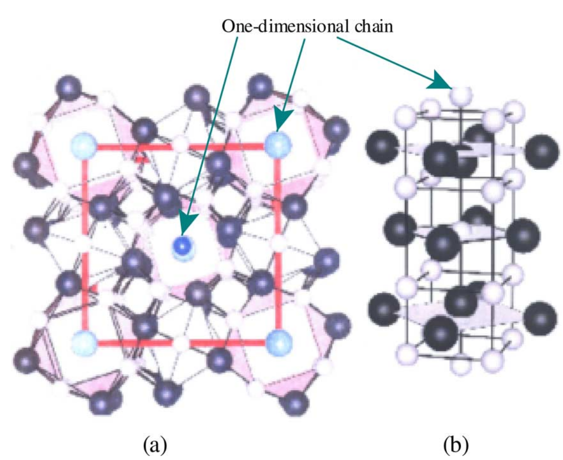


Fig. 4. Peak temp. (Tp) versus applied field, between zero and 31.85 kA/m.



(a) (b)

Fig. 5. Two views of the crystal structure of Zr_9Ni_{11}: (a) along the c-axis. and (b) normal to the c-axis. From Stalick, *et al.* [1].

from the Dzyaloshinskii-Moriya interactions [4], [5] occurring in the Zr_9Ni_{11} compound. In fact, the crystal structure study conducted on the Zr_9Ni_{11} compound by neutron diffraction, carried out in the range of 4 K and 1273 K, and the selected-area electron diffraction (SAED) and convergent beam Transmission electron microscope, TEM, analyses showed that the compound had a Zr_9Pt_{11}-type tetragonal structure with columnar atomic chains of alternating Zr and Ni atoms parallel to the c axis [1]; these atomic chains reside within the tetragonal structure and are shown schematically in Fig. 5. Changes observed in the neutron diffraction spectra, occurring over time but at constant temperatures, have been shown to be caused by the movements of

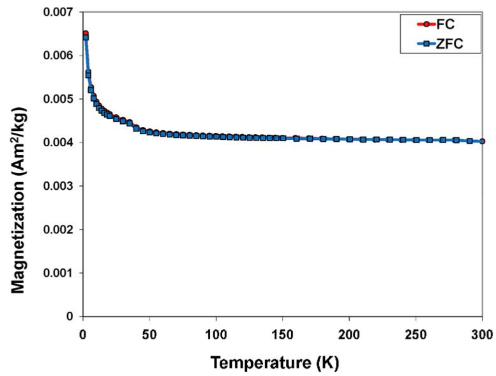


Fig. 6. M_{ZFC} (circles) and M_{FC} (squares) versus T plots at 79.62 kA/m for ZrNi equiatomic compound.

the atoms along the chains over short distances [1]. These atom movements are consistent with the magnetic results obtained in this study. Specifically, the fluctuations that are present in the M_{FC} versus T plot at 31.85 kA/m are believed to be the result of the same small movements of the atoms along the chains that give rise to the changes that were observed in the neutron diffraction spectra [1].

In Fig. 6 are presented the M_{ZFC} and M_{FC} versus T plots for the equiatomic ZrNi compound for an applied field $H = 79.62$ kA/m. As it may be observed from the figure, the M_{ZFC} and M_{FC} versus T plots are nearly identical and they both exhibit a sharp increase in the magnetization in the low temperature region (i.e., below 35 K). From both the microstructural and chemical analyses conducted on Zr_9Ni_{11} compound it was estimated that it contained about 10% ZrNi minority phase [1]. Therefore, it is believed that the upturn seen in magnetization values, especially in the M_{FC} versus T plots in the low temperature region (Figs. 1, 2, and 3) is due to the presence of the ZrNi minority phase in the Zr_9Ni_{11} compound.

IV. Concluding Remarks

Using SQUID magnetometry, magnetic measurements were conducted on the Zr_9Ni_{11} intermetallic compound from 2 K to 320 K. Examination of the M_{ZFC} and M_{FC} versus T plots showed that the compound displays an unusual behavior that includes: a spin glass behavior, zero-field-magnetization curves lying above the corresponding field-cooled magnetization curves, and the presence of fluctuations in the field-cooled magnetization curves. A parallel structural study conducted on the same compound showed that the Zr_9Ni_{11} compound consists of a host periodic structure with structurally disordered one-dimensional chains that are weakly correlated with each other. Furthermore, variation of atom positions within these chains can occur from room temperature down to 4 K. These structural variations provide the basis for explaining the unusual magnetic behavior observed in the Zr_9Ni_{11} compound.

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