Magnetic and Structural Properties of the Amorphous Material Ni_2SnTe_4

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In recent years there has been an increasing interest in the study of amorphous materials. Amorphous solids differ from crystalline ones in that they lack the long-range translational order characteristic of crystalline solids. This affects the optical, electronic and magnetic properties of these solids. These unique characteristics of amorphous materials have suggested potential applications in electronics, photovoltaics, catalysis, and optical and magnetic materials [1, 2]. In addition to the unique applications resulting from their structure and related properties, amorphous materials also often allow control of composition, surface area and ordering, which is not possible in crystalline materials.

We have recently been studying the magnetic properties of several amorphous materials that exhibit spin glass behavior. A spin glass is a magnetic material that is characterized by a random freezing of the magnetic moments at a well-defined temperature called the freezing temperature, T_f [3]. In the system M_2SnTe_4, we have prepared and characterized materials with M = Cr, Mn, Fe and Co. They are prepared by the metathesis reaction between the metal halides and the ternary Zintl phase material K_4SnTe_4 in methanol. The compounds are formed as air-sensitive amorphous materials that decompose to simpler metal tellurides upon heating [4]. Because of their metastable nature, preparation of these materials by more conventional high-temperature techniques would be impossible. The chromium, manganese, iron and cobalt analogs all show spin glass behavior with T_f equal to 16, 13, 12 and 5 K, respectively [5–7]. It has also been found that magnetic bubbles can be formed in the spin glass medium of Fe_2SnTe_4 upon irradiating the zero-field-cooled compound with ultraviolet light at 5 K [8].

During our recent study of the cobalt and nickel compounds [7], we noted that the magnetic properties of the cobalt compound were dependent on preparation conditions. In this paper we report that the nickel system also demonstrates preparation-dependent magnetic properties and that this material may be synthesized as a spin-glass or an itinerant ferromagnet.

Experimental

Synthesis

Due to the extreme oxygen sensitivity of these compounds, all manipulations were carried out in an argon-filled glovebox containing less than 1 ppm oxygen. K_4SnTe_4 was prepared by the reaction of KSn and tellurium, as described previously [9]. Ni_2SnTe_4 was prepared by the reaction of methanolic solutions of nickel(II) chloride and K_4SnTe_4. To various volumes of methanol (Reagent grade, degassed), 1.00 g of K_4SnTe_4 was added. Similarly, 0.33 g of $NiCl_2$ (Reagent grade) was dissolved in various volumes of methanol. A single drop of distilled, degassed water was added to the nickel solutions to increase solubility of the chloride. While stirring the nickel solution, stoichiometric quantities of the K_4SnTe_4 solutions were added. A fine, black precipitate was immediately formed. It was separated by suction filtration, washed with methanol and dried overnight over P_2O_5.

X-ray Analysis

The X-ray fluorescence spectrum of each of the samples was recorded in order to verify whether the materials had the same stoichiometric composition. All of the preparations had identical X-ray fluorescence spectra.

Magnetism

The magnetic measurements were conducted on a SHE Corp. VTS-50 superconducting SQUID susceptometer that was interfaced to the IBM 9000 computer system. Measurement and calibration techniques have been reported elsewhere [10]. The types of experiments that were conducted are the measurement of the susceptibility as a function of temperature, and the magnetization as a function of field.

Electron Microscopy

High-resolution electron micrographs were recorded on the KRATOS EM-1500 high-voltage electron microscope at the National Center for Electron Microscopy at Lawrence Berkeley Laboratory. This microscope allows resolution to the 0.3 nm level. Microanalysis was obtained with a JEOL AEM 200CX analytic electron microscope operating in the STEM mode and equipped with the KEVEX system 8000.

Results and Discussion

Ni_2SnTe_4 is prepared as a pyrophoric, amorphous powder by the reaction of methanol solutions of nickel chloride and K_4SnTe_4. The amorphous nature

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can be seen by powder X-ray diffraction. The X-ray fluorescence spectra of all of the samples that we examined are identical, verifying the uniformity of the stoichiometry within the experimental error of the instrument (±5%).

Magnetic susceptibility measurements were conducted on various preparations of Ni_2SnTe_4. Figure 1 shows a plot of the susceptibility versus temperature for a sample prepared from a 0.10 M solution of $NiCl_2$ and a 0.075 M solution of K_4SnTe_4. The differences in the susceptibility of the sample cooled in zero field and the sample cooled in the measuring field are characteristic of a spin glass with a freezing temperature of 7 K. When the sample is prepared from solutions with a lower concentration of nickel chloride (greater volume of methanol used to prepare the solution) and a higher concentration of K_4SnTe_4, a freezing temperature of approximately 3 K is seen

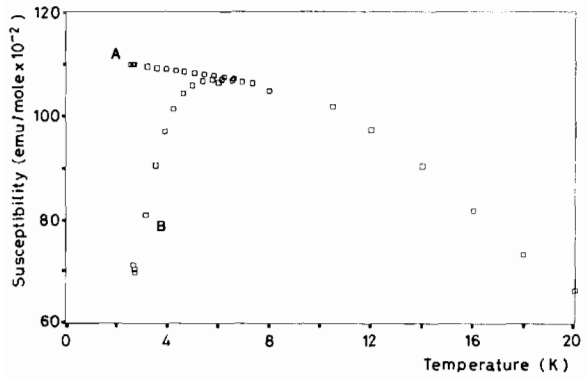

Fig. 1. The magnetic susceptibility plotted as a function of temperature, in a measuring field of 1.0 kOe, for a sample of Ni_2SnTe_4 prepared from a 0.10 M nickel chloride solution and a 0.075 M K_4SnTe_4 solution. Two experiments are illustrated. Curve (A) illustrates the behavior of the sample when cooled in the measuring field; curve (B) shows the behavior when cooled in zero field.

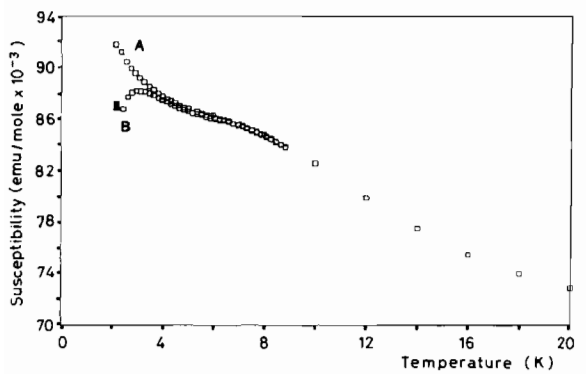

Fig. 2. The magnetic susceptibility plotted as a function of temperature for a sample prepared from a 0.025 M nickel chloride solution and a 0.16 M K_4SnTe_4 solution. Curves (A) and (B) are field cooled and zero-field cooled, respectively.

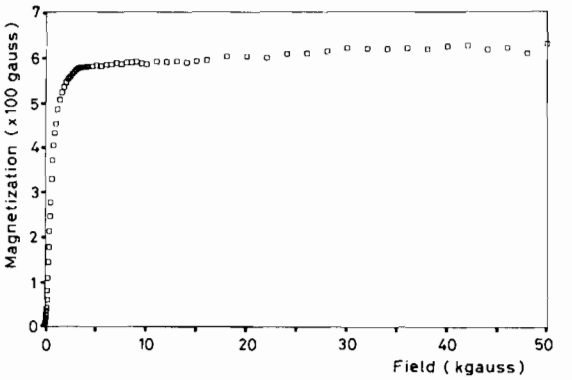

Fig. 3. The magnetization versus field for a sample of Ni_2SnTe_4 prepared from unstirred solutions of 0.10 M $NiCl_2$ and 0.075 M K_4SnTe_4.

(Fig. 2). If the nickel chloride solution is not stirred during the addition of the K_4SnTe_4 solution, an itinerant ferromagnet (as shown in Fig. 3) is produced.

Samples of Ni_2SnTe_4 were also examined by electron microscopy to determine the micro-structure, composition and uniformity of these materials. The separate elemental analyses were the same within experimental error (±2%). Analytical electron microscopy analysis of the 7 K spin glass sample gave the following elemental analyses. *Anal.* Found: Ni, 20.6, Sn, 16.0, Te, 63.4. Calc. for Ni_2SnTe_4: Ni, 15.7; Sn, 15.9; Te, 68.4 wt%. These data indicate the samples to be slightly nickel-rich compared to the expected Ni_2SnTe_4 formula. Since the curious behavior of the magnetic data could be explained by varying the crystallite sizes and composition of a multiphased system, an analytical line scan was performed to determine the microscopic compositional uniformity of the materials. A particle of *c.* 0.8 μm from the same sample was scanned in the STEM mode with the JEOL 200CX AEM using an electron probe beam of about 200 Å cross-section. Elemental analysis was obtained by recording and analyzing the X-ray fluorescence of the excited region with the KEVEX 8000 analysis programs. Figure 4 shows a plot of the composition of a single particle of Ni_2SnTe_4 as a function of distance across the particle. Within experimental error, the composition of this particle is uniform. Furthermore, all particles that were examined from this preparation had the same elemental composition within experimental error.

The amorphous nature of the Ni_2SnTe_4 is confirmed by both electron diffraction and transmission electron microscopy. Ultra-high-resolution electron microscopy could not resolve any structural order at magnifications to the resolution of the instrument (*c.* 5 Å).

It appears that the magnetic properties of Ni_2SnTe_4 are, like the cobalt analog, dependent upon

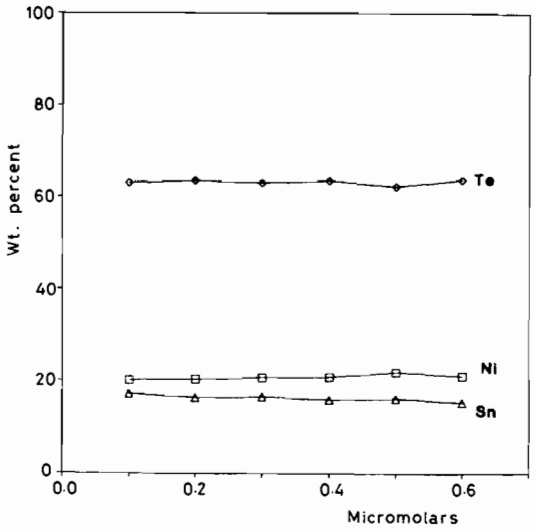

Fig. 4. The weight percent composition of nickel, tin and tellurium as a function of distance across a single particle of Ni_2SnTe_4 as determined by electron microprobe line analysis, as described in the text.

the exact preparation conditions. It is still unclear as to the exact cause of this dependence, although the data presented in this report rule out inhomogeneities or gross compositional differences.

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