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# Spin glass behavior in some ternary metal chalcogens

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**Abstract.** The magnetic properties of some amorphous metallic materials of the formula $M_2SnTe_4$, where M = Cr, Mn, and Fe, are presented. The materials exhibit anomalous magnetic behavior at low temperatures. The field cooled and zero field cooled d.c. magnetic susceptibilities show different behavior when measured below the transition temperature. The materials exhibit a thermal remanent magnetization and isothermal remanent magnetization that is consistent with that of a spin glass. The spin glass freezing temperatures for these materials are 18 K, 11 K, and 12 K for M = Cr, Mn, and Fe, respectively.

**Keywords.** Spin glass behavior; ternary metal chalcogens; magnetic properties, amorphous metallic substances.

## 1. Introduction

In two previous communications, we described the synthesis and characterization of a series of ternary metal chalcogens of the formula $M_2SnTe_4$ where M = Cr, Mn, Fe, and Co (Haushalter *et al* 1984a,b). The zero field variable temperature electrical conductivities of these materials have also been studied (Goshorn *et al* 1986). These new materials exhibit some remarkable properties including resistivity ranging from $10^4$ to $10^{-4}$ (ohm-cm), a spin glass "transition" at temperatures ranging from 5 to 18K, and amorphous structure down to the 10Å level. In addition, some novel reactions of the precursor ternary Zintl phase materials with polyimide plastics have been described (Haushalter 1983; Haushalter and Krauss 1983).

The preparation of the ternary metal chalcogens involves a metathesis reaction between a Zintl phase material ($K_4SnTe_4$) and a divalent transition metal bromide. The Zintl phase results from the interaction between the less electronegative metals (i.e., alkali and alkaline earth metals) and the more electronegative metals and metalloids (i.e., the post-transition metals). There are several reviews that describe the properties of the Zintl phase materials (see for example, Shafer *et al* 1973; Corbett 1985). The Zintl phase of matter can be described as a polar metallic alloy in which the bonds have a substantial amount of ionic character. The ionic character of the Zintl phase is often sufficient to allow for the solvation of salt-like ions in polar solvents (e.g., KSn dissolves in liquid $NH_3$ and $K_4SnTe_4$ dissolves in $H_2O$).

The transition metal tin tellurides are prepared from the Zintl phase material $K_4SnTe_4$. The ionic character of $K_4SnTe_4$ permits the Zintl phase alloy to form an aqueous ionic solution as shown in (1).

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$$K_4SnTe_4\ (s) \xrightarrow[R=H,\ CH_3]{ROH} 4K^+ + SnTe_4^{4-} \tag{1}$$

This material is quite reactive and, in the presence of a metal cation of sufficient electron affinity, will form an insoluble metallic alloy of formula $M_2SnTe_4$ due to the transfer of electrons from the $SnTe_4^{4-}$ ion to the metal following reaction (2).

$$2M^{+2} + SnTe_4^{4-} \longrightarrow M_2SnTe_4\ (s) \tag{2}$$

X-ray powder diffraction patterns exhibit a lack of long range crystalline order for the freshly prepared material. Subsequent neutron diffraction verified the glassy amorphous nature of the materials. Since these materials show a tendency to decompose at higher temperatures (*vide infra*), high temperature techniques such as rapid thermal quenching could not be used to produce these amorphous materials. Also sputtering techniques would not be expected to generate the $SnTe_4$ tetrahedra.

The first clue to the unusual magnetic properties of these materials came from the Mossbauer experiment (Haushalter *et al* 1984b). These experiments revealed the presence of a large moment in the freshly prepared material at low temperature resulting from ordered spins on both the iron and the tin atoms. This implies that the electrons are somewhat delocalized. Magnetic susceptibility experiments verified the existence of the spin glass state in these materials.

Over the past fifteen years, the spin glass phenomenon has grown into a sizable area of research in solid state science (see, for example, Moorjani and Corey 1985; Edwards and Anderson 1975, 1976; Fisher 1983, 1985). The spin glass problem provides a testing ground for the theories that attempt to address many intriguing questions concerning amorphous structure and magnetism, the nature of the spin glass state, and the relation of the spin glass transition to critical phenomena.

There are several reviews that discuss the theory, and concept of the spin glass phenomenon, as well as the many reports of experimental studies on spin glasses (for a recent review see, Moorjani and Corey 1985; or Fisher 1983, 1985). The spin glass phenomenon first came to prominence following reports by Mydosh and coworkers that a cusp in the AC susceptibility of AuFe was observed at a well-defined temperature (Cannella *et al* 1971). These initial reports did not mention a frequency dependence of the temperature of the cusp in the susceptibility and it was thought a phase transition to a new state had occurred (Edwards and Anderson 1975). However, subsequent reports on other complexes showed a significant dependence of peak height and temperature on the ac frequency.

Another curious feature of spin glass systems is the marked difference between the AC and DC susceptibility. The DC susceptibility is very dependent on the manner in which the experiment is performed (Guy 1979). For example, a zero field cooled specimen shows very different behavior from a field cooled specimen, and even the rate of cooling of a field cooled sample has an effect on the response of the sample to a DC susceptibility measurement below the spin glass temperature. These observations are inconsistent with the usual concept of phase transition. In addition to the curious magnetic behavior, other experiments, for example heat capacity (Wenger and Keesom 1975, 1976) and conductance

(Laborde and Radakrishna 1973; Ford and Mydosh 1980), were also difficult to reconcile to a phase transition model. As a result, the term "spin glass" was coined to describe the emerging magnetic effects that had an uncanny resemblance to the behavior observed in real glass systems. Current theories are again developing that support the phase transition model, but there is still a great deal of speculation and controversy over whether an equilibrium state even exists (see for example Fisher 1985; Souletie 1985).

In this report, we describe the d.c. magnetic susceptibility and remanent magnetization experiments on the complexes $M_2SnTe_4$, where M = Cr, Mn, Fe. These complexes exhibit properties consistent with the spin glass state. The spin glass freezing temperatures are in the range 12–18 K.

## 2. Experimental

*Syntheses*: All of the materials are extremely air sensitive. Preparation and sample manipulations were performed under an argon atmosphere.

$K_4SnTe_4$: The ternary Zintl material $K_4SnTe_4$ was prepared as described earlier (Huffman *et al* 1984).

$M_2SnTe_4$: Methanolic solutions containing a stoichiometric amount of the transition metal bromides were mixed with methanolic solutions of $K_4SnTe_4$ and the product material $M_2SnTe_4$ immediately formed as a metallic black precipitate. The black precipitate was filtered, washed with ethanol, and dried in vacuum overnight.

*Magnetic measurements*: Variable temperature magnetization measurements were recorded on a SHE Corporation Superconducting SQUID susceptometer. Measurement and calibration techniques are reported elsewhere (O'Connor 1982).

## 3. Results and discussion

The d.c. magnetic susceptibility of each of the samples deviated greatly from Curie-Weiss behavior. At the lowest temperatures, the magnetic data of these materials exhibited anomalous magnetic behavior consistent with a magnetic phase transition. The spin glass character of the material became evident when different environments of sample cooling were used.

Figure 1 illustrates the low temperature d.c. magnetic susceptibility for $Mn_2SnTe_4$. Two experiments are included in this plot. First the sample was cooled in a magnetic field ($H_c$ = 10 mT) and then measured in the same field ($H_m$ = 10 mT). The magnetic data are plotted as a function of temperature up to 100 K. The inset shows the magnetic response of the sample when it is cooled in a zero magnetic field ($H_c$ = 0) and then measured in an applied magnetic field ($H_c$ = 10 mT). Difference in these data sets is expected for a material with a spin glass transition at a freezing temperature $T_f \approx 12$ K.

The iron and chromium analogs also exhibit this phenomenon. For example, figure 2 shows the magnetic response of $Fe_2SnTe_4$ over the 5 to 20 K temperature region. In these experiments, the same measuring field ($H_m$ = 10 mT) is again used. For one data set the sample was cooled in a zero magnetic field ($H_c$ = 0) and

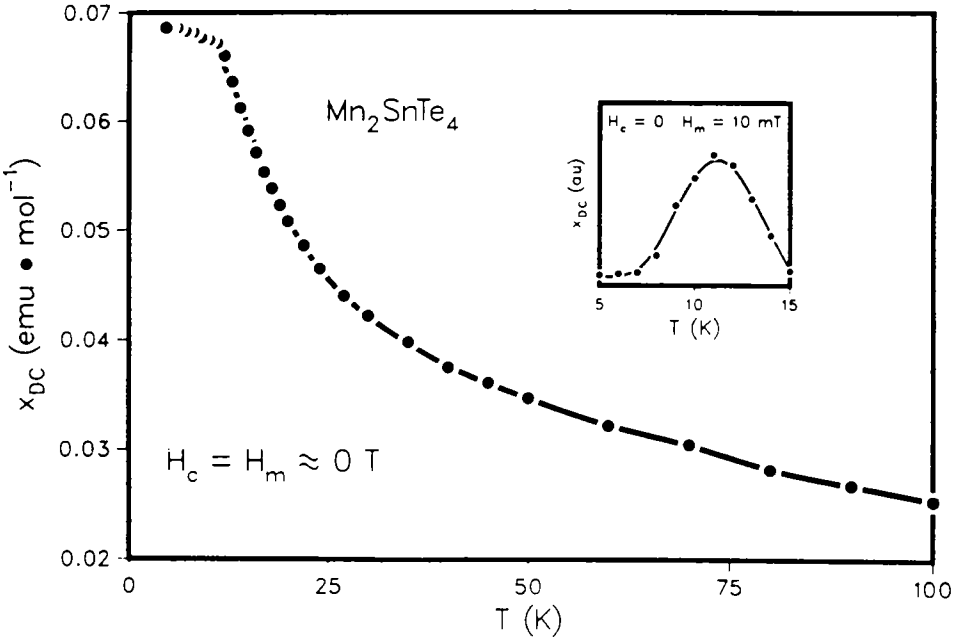


**Figure 1.** A plot of the d.c. magnetic susceptibility of $Mn_2SnTe_4$. The sample was frozen and measured in a field of 10 mT. The inset illustrates the magnetic response of a sample frozen at zero field and then measured at 10 mT.

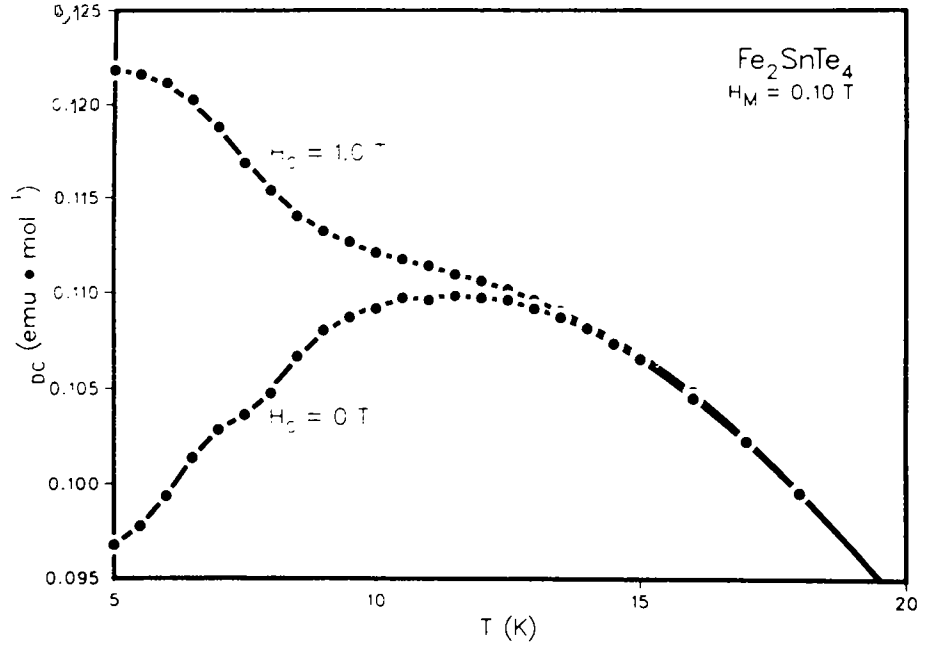


**Figure 2.** A plot of the magnetic susceptibility as a function of temperature for $Cr_2SnTe_4$. The two curves at low temperature illustrate the effect of zero field cooling (lower curve) and high field (1·0 T) cooling (upper curve). The two curves merge in the paramagnetic domain above the spin glass freezing temperature.

for the other data set the sample was cooled in a large magnetic field ($H_c$ = 1 T). When the spin glass is cooled in a zero field, the spins are frozen in a random orientation. The spins try and maintain their random frozen alignment when the measuring field is turned on. As the spin glass freezing temperature is passed, the spins begin to "melt" and the paramagnetic phase is entered.

When the spin glass is cooled in a large applied field ($H_c$ = 1·0 T), the spins freeze in alignment with the applied magnetic field. The frozen spins try to maintain this alignment even when the field is reduced. This results in a measured d.c. susceptibility that is larger than the value measured for the zero field cooled specimen. At temperatures above the spin glass freezing temperature, there is no difference between the magnetic response for each of the cooling experiments.

The spin glass freezing temperatures are listed in table 1 for the complexes $M_2SnTe_4$, where M = Cr, Mn, and Fe. Also listed in table 1 are the conductivities and standard reduction potentials for these materials. The degree of metallic character (conductivity) appears to show some correlation with the reduction potential of the metal ions in solution (Goshorn *et al* 1986). This correlation is not as striking for the spin glass freezing temperatures but does show a general trend. A better correlation should be apparent upon a comparison of electron affinities in the solid state. For comparison, the oxidation potential of $SnTe_4^{4-}$ has been estimated by chemical means to be 0·7 ± 0·2 V.

There are three general approaches to describing the spin glass phenomenon. The first general approach is the Neél description. This is an analogy with superparamagnetism in which domains of random moments are connected by free spins. A thermodynamic blocking equilibrium is then achieved via a mechanism called the RKKY interaction, and a random locking of the moments occurs at $T_f$. The second approach to understanding the spin glass phenomenon proposes a regular lattice of spins with random degrees of coupling forces, usually a Gaussian probability of interaction strengths. The most attractive feature of this model is the simplicity of the theory and its lending itself to the calculation of critical exponents. The third approach is the "window glass" analogy to the freezing of structural glasses. This analogy gave rise to the term spin glass and is consistent with many of the properties observed. This model does not predict a distinct phase transition but rather a gradual change in the viscosity of the spins as the moments are less able to follow an external magnetic field. The major advantage of this approach is that it is very easy to grasp the concept of the spin glass on an intuitive level. Although some of the predictions of these theories occasionally agree, the theories often contradict

**Table 1.** List of standard reduction potentials ($M^{+2} + 2e^- \longrightarrow M$), resistivity ($\rho$), and spin glass freezing temperatures for $M_2SnTe_4$, M = Cr, Mn and Fe.

| M | $E^\circ$ (volts) | $\rho$(ohm cm) | $T_f$ (K) |
|---|---|---|---|
| Cr | −0·559 | – | 18 |
| Mn | −1·029 | $3 \times 10^4$ | 11 |
| Fe | −0·409 | $9 \times 10^{-4}$ | 12 |

one another and each has serious shortcomings in its ability to explain all the facts of the spin glass state.

The spin glass phenomenon is characterized by some very unusual behavior in the bulk magnetic properties of the materials. The electrons ability to follow a magnetic field is drastically modified by the onset of the spin glass state. The freezing of the moments can result in a large remanent magnetization in the material. Perhaps the most diagnostic experiment for the characterization of the spin glass state is the analysis of the field dependence of the isothermal remanent magnetization and thermal remanent magnetization.

*Isothermal remanent magnetization (IRM)*: This experiment involves cooling the specimen in a zero field to temperatures below the spin glass freezing point. The onset of the spin glass phase then results in a freezing of the magnetic moments in a truly random fashion since no external force was present for the spins to align with. The specimen is then exposed to an applied magnetic field. After a certain time, the applied field is quenched and the resultant magnetization is measured in zero applied magnetic field. Under these conditions an ideal spin glass would show zero magnetization since the spins would remain frozen randomly throughout the bulk of the specimen.

*Thermal remanent magnetization (TRM)*: This experiment on the other hand exhibits vastly different magnetic behavior. In the TRM experiment the specimen is cooled to a temperature below the spin glass freezing temperature while in an applied magnetic field. The spins, which had a tendency to align with the applied magnetic field while in the paramagnetic phase, are now frozen into a position of partial alignment with the applied field. While the specimen is in the frozen spin glass state, the magnetic field is quenched. Since the spins are frozen, their alignment is not quenched and a resultant moment is present in the material. The TRM measurement should give a large remanent relative to the IRM.

The TRM, IRM experiment for $Cr_2SnTe_4$ is illustrated in figure 3. The hump in the TRM curve has been observed in many spin glasses and is characteristic of the spin glass state; nevertheless, this anomaly escapes theoretical explanation. The two curves begin to converge at fields near 1·0 T indicating that the spin glass state is destroyed by high fields.

The effect of the TRM is greatly enhanced by performing the experiment at lower temperatures. Figure 4 illustrates a plot of ln TRM as a function of temperature. In TRM values of $-3$ are negligible and may be assumed to represent the absence of a magnetic remanence. This indicates that the paramagnetic phase dominates.

Another important property of spin glasses is their time dependence. A log/log plot of the TRM of $Fe_2SnTe_4$ as a function of the time exhibits a straight line. The initial thermal remanent magnetization is therefore transient because of a large reversible component. But the TRM then begins to approach a quasi-steady state value after a few minutes. Figure 5 illustrates this behavior for $Fe_2SnTe_4$.

The RKKY interaction, bond disorder, topological disorder, and impurity centers are all candidates for the source of the frustration that is necessary for the spin glass state to exist. The RKKY interaction is the primary cause of frustration in conducting amorphous materials such as the dilute noble metal alloys. The phase dependence of the interaction causes the frustration necessary for blocked spin

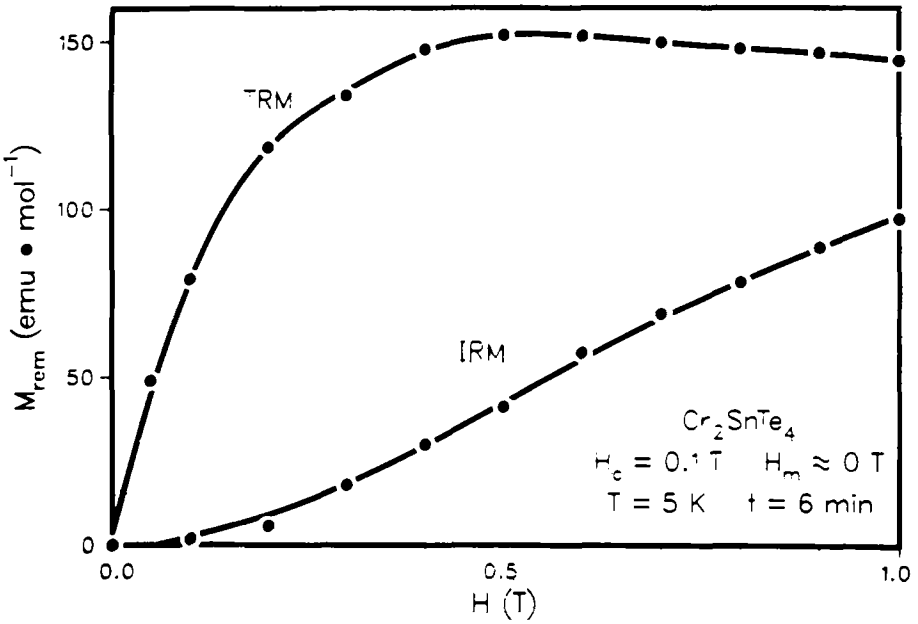


**Figure 3.** A plot of the IRM and TRM as a function of magnetic field for $Cr_2SnTe_4$.

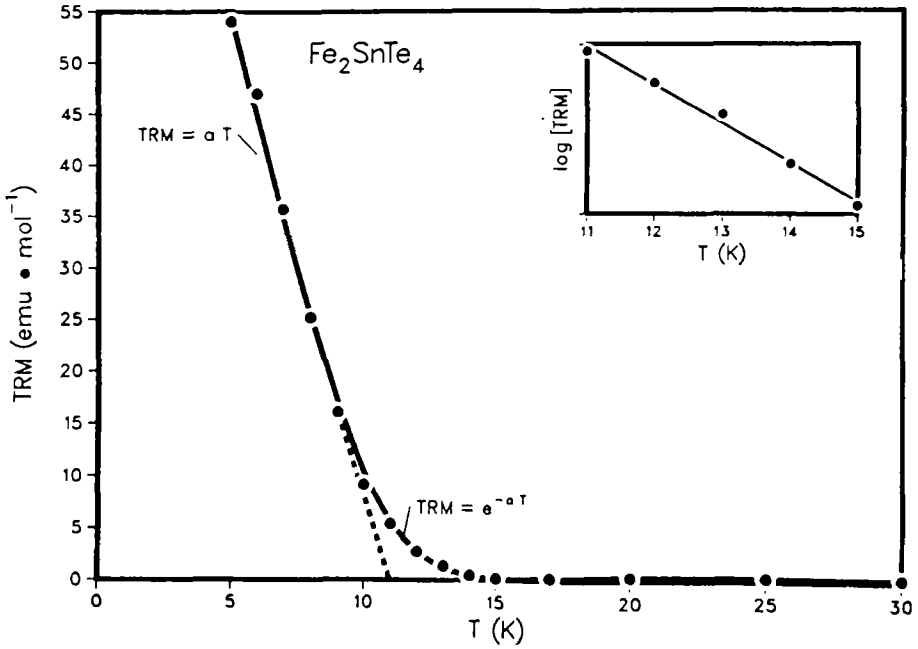


**Figure 4.** Plots of the TRM of $Fe_2SnTe_4$ plotted as a function of the temperature. Extrapolation of the TRM to zero is used to obtain the spin glass freezing temperature.

fluctuation and finally results in the freezing of the spins in their random positions. Bond disorder, topological disorder, or a combination of the two phenomena are also causes of frustration in amorphous materials. The random variance of the

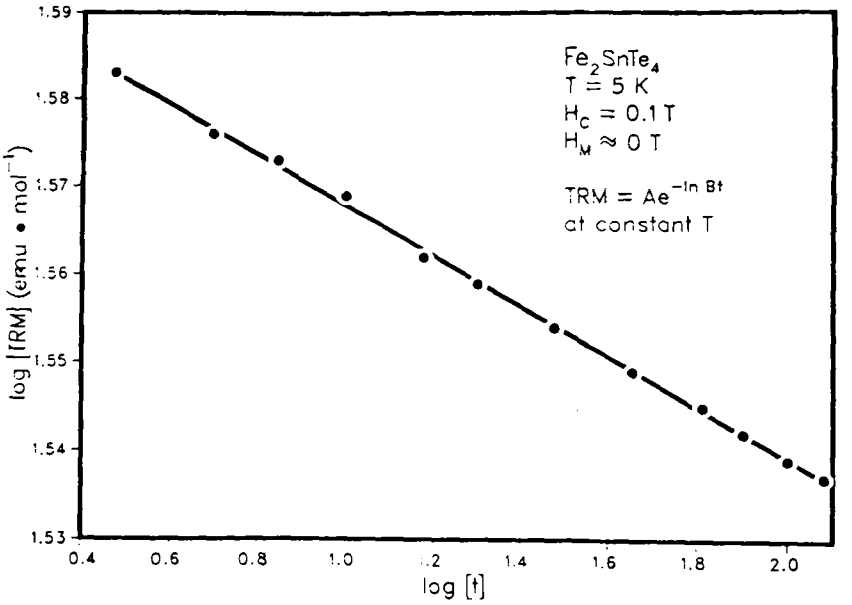


**Figure 5.** A log/log plot of the TRM of $Fe_2SnTe_4$ as a function of the time.

interactions in the three dimensional solid produces the frustration necessary for the spin glass phase. The spin glass "phase" often occurs in amorphous materials. However, the frustration of exchange interaction necessary for the spin glass state may also occur as the result of impurity centers in a crystal lattice.

The source of the frustration in these materials is likely due to a combination of bond disorder and topological disorder. The solid material has been reported to be a glassy metallic material that exhibits very little crystalline order. The material is also thermodynamically unstable with respect to the formation of the metal tellurides and the tin tellurides. For example, $Fe_2SnTe_4$ exhibits a powder pattern consistent with poor crystalline order. After heating this material for 24 hours at 600°C, the powder pattern exhibits peaks which may be indexed as $FeTe_x$ and SnTe (Haushalter *et al* 1984a). The freshly prepared material exhibits spin glass behavior, as shown in figure 2, while the heat treated material exhibits an antiferromagnetic transition with a $T_N \sim 90$ K, as shown in figure 6.

Several forms of iron tellurium alloys ($FeTe_x$) have been reported and these alloys exhibit a variety of magnetic properties (Hullinger 1968). For example, an alloy of stoichiometry $FeTe_{1.1}$ exhibits normal Curie-Weiss behavior (Suchet and Serre 1965). Another alloy of stoichiometry $FeTe_{0.95}$ exhibits antiferromagnetism with $T_N = 63$ K (Tsubokawa and Chiba 1959; Naya *et al* 1960). Some alloys of iron and tellurium with integral stoichiometric coefficients include FeTe which is an antiferromagnetic material with $T_N = 70$ K (Anon 1963), $FeTe_2$ which is also antiferromagnetic with $T_N = 83$ K (Llewellyn and Smith 1959), and $Fe_9Te_8$ which has a transition temperature $T_c = 63$ K and exhibits ferromagnetism above this temperature and ferrimagnetism below this temperature (Gronvold *et al* 1954). It is likely that we have prepared a phase that is related to the $FeTe_2$ phase, but with slightly different stoichiometry that permits increase in the Neel temperature to approximately 90 K.

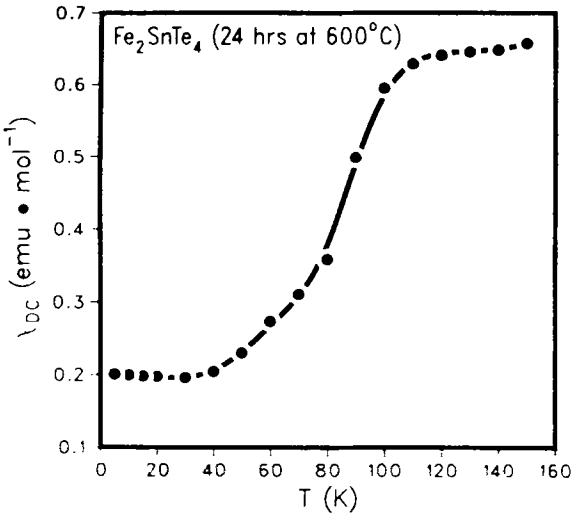


**Figure 6.** The magnetic susceptibility of a sample of $Fe_2SnTe_4$ after it was heat treated for 24 hours at 600 K. The freshly prepared material is amorphous, while the heat treated material behaves as a mixture of $FeTe_x$ and SnTe, where the antiferro-magnetism is attributed to $FeTe_x$.

It is possible that the spin glass interactions in $Fe_2SnTe_4$ are the result of a frustration of the FeTe interactions. However, it is generally believed that the frustration necessary for a spin glass phase must result in an order of magnitude reduction in the ordering temperature (Moorjani and Corey 1985).

## 4. Conclusion

The materials of the formula $M_2SnTe_4$ are amorphous metallic alloys that exhibit a wide range of conductivities. These materials exhibit magnetic remanence and time dependence consistent with the spin glass state. The heated $Fe_2SnTe_4$ exhibits an antiferromagnetic transition at $T_N \sim 90$ K consistent with $FeTe_x$ and SnTe decomposition products. The metallic character as measured by the conductivity shows a dependence on the reduction potential of the transition metal ion in solution. The properties of other magnetic systems prepared from $K_4SnTe_4$ will probably also provide systems that exhibit interesting magnetic behavior.

## References

Anon 1963 *American Institute of Physics Handbook* 2nd edn (New York: McGraw Hill) pp. 5-200
Cannella V, Mydosh J A and Budnick J I 1971 *J. Appl. Phys.* **42** 1689
Corbett J D 1985 *Chem. Rev.* **85** 383
Edwards S F and Anderson P W 1975 *J. Phys.* **F5** 965
Edwards S F and Anderson P W 1976 *J. Phys.* **F6** 1927
Fisher K H 1983 *Phys. Status Solidi* **B116** 353
Fisher K H 1985 *Phys. Status Solidi* **B119** 130
Ford P J and Mydosh J A 1980 *Phys. Rev.* **B21** 1902
Goshorn D P, Sewchok M G, Roxlo C B and Haushalter R C 1987 *Inorg. Chem.* (submitted)

Gronvold F, Haraldses H and Vihorde J 1954 *Acta Chem. Scand.* **8** 1927
Guy C N 1979 *J. Appl. Phys.* **50** 7308 and references therein
Hullinger F 1968 *Struct. Bonding (Berlin)* **4** 63
Haushalter R C 1983 *Angew. Chem.* **95** 560
Haushalter R C and Krauss L J 1983 *Thin Solid Films* **102** 2312
Haushalter R C, O'Connor C J, Haushalter J P, Umarji A M and Shenoy G K 1984 a *Angew Chem.* **96** 147
Haushalter R C, O'Connor C J, Umarji A M, Shenoy G K and Saw C 1984b *Solid State Chem.* **49** 929
Huffman J C, Haushalter J P, Umarji A M, Shenoy G K and Haushalter R C 1984 *Inorg. Chem.* **23** 2312
Laborde O and Radakrishna P 1973 *J. Phys.* **F3** 1731
Llewellyn J and Smith T 1959 *Proc. Phys. Soc.* **74** 65
Moorjani K and Corey J M D 1985 *Magnetic glasses* (Amsterdam: Elsevier)
Naya R, Murahami M and Hirahara E 1960 *J. Phys. Soc. Jpn.* **15** 360
O'Connor C J 1982 *Prog. Inorg. Chem.* **29** 203
Shafer H, Eisenmann B and Muller H 1973 *Angew. Chem. Int. Ed. Engl.* **12** 694 and references therein
Souletie J 1985 *Ann. Phys. (Paris)* **10** 69
Suchet J and Serre J 1965 *C. R. Acad. Sci. Paris* **260** 3890
Tsubokawa I and Chiba S 1959 *J. Phys. Jpn.* **14** 1120
Wenger L E and Keesom P H 1975 *Phys. Rev.* **B11** 3497
Wenger L E and Keesom P H 1976 *Phys. Rev.* **B13** 4053