

H<sub>2</sub>O content in the starting solutions. Larger amounts of HCl in the starting solution gave rise to the formation of monolithic opaque gels with larger particles and accordingly larger open pores. It was argued that particles in the solutions do not form rigid, highly cross-linked polymers

as in base-catalyzed solutions but form round-shaped secondary particles composed of linearly polymerized primary particles.

Registry No. TMOS, 681-84-5.

## A New Amorphous Magnetic Material: Fe<sub>5</sub>(InTe<sub>4</sub>)<sub>2</sub>

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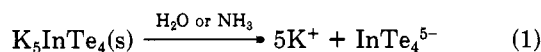
Received December 5, 1988

A new ternary Zintl material of the formula K<sub>5</sub>InTe<sub>4</sub> has been prepared. This material undergoes a metathesis reaction with ferrous chloride in aqueous solution to produce the alloy Fe<sub>5</sub>(InTe<sub>4</sub>)<sub>2</sub>. The dc magnetic susceptibility of Fe<sub>5</sub>(InTe<sub>4</sub>)<sub>2</sub> is reported and is consistent with a spin glass having a freezing temperature of T<sub>f</sub> = 15 K. The isothermal and thermal remanent magnetization experiments are also described. The ac magnetic susceptibility has been measured as a function of frequency and temperature and exhibits a broad maximum with two humps occurring at 15 and 32 K.

### Introduction

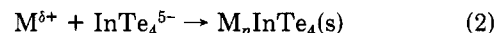
Zintl phases are combinations of metals and/or metalloids in which large differences in electronegativity result in a substantial amount of ionic character in the bonds.<sup>2,3</sup> A ternary Zintl material K<sub>4</sub>SnTe<sub>4</sub> has been prepared<sup>4</sup> and has been shown to react with divalent transition-metal cations in methanolic solution to produce amorphous alloys of the formula M<sub>2</sub>SnTe<sub>4</sub>, M = Cr, Mn, Fe, Co, and Ni. Recent studies of these alloys have shown them to exhibit spin glass behavior,<sup>5-9</sup> unusual photomagnetic effects,<sup>10</sup> a wide range of electrical resistivities,<sup>11</sup> and form thin films on polyimide plastics.<sup>12,13</sup>

We have now prepared a new ternary Zintl phase material, K<sub>5</sub>InTe<sub>4</sub>. The ionic character of K<sub>5</sub>InTe<sub>4</sub> permits the Zintl phase to form an ionic solution in polar solvents such as water and liquid ammonia, as shown in (1).



In the presence of a transition-metal cation of sufficient electron affinity, this material will form an insoluble

metallic alloy of formula M<sub>n</sub>InTe<sub>4</sub> due to the redistribution of charge between the InTe<sub>4</sub><sup>5-</sup> anion and the metal cation following reaction 2, where the stoichiometric coefficient



n is determined by the charge δ on the metal cation as well as other reduction characteristics of the solution. In this report, we describe the synthesis and characterization of a new amorphous magnetic material, Fe<sub>5</sub>(InTe<sub>4</sub>)<sub>2</sub>, which forms from the reaction of the Zintl phase material, K<sub>5</sub>-InTe<sub>4</sub>, with FeCl<sub>2</sub> in an aqueous solution.

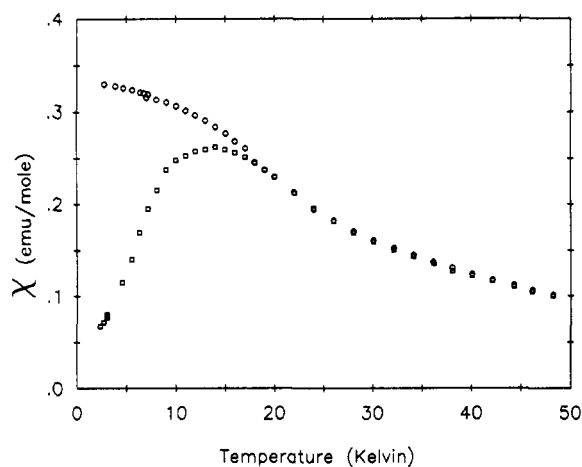
### Experimental Section

**Synthesis.** Due to the extreme sensitivity of these compounds, all manipulations were carried out in an argon-filled glovebox containing less than 1 ppm of oxygen.

**K<sub>5</sub>InTe<sub>4</sub>.** The binary Zintl phase K<sub>5</sub>In<sub>8</sub> was prepared by mixing molten potassium with molten indium in a stoichiometric ratio in a quartz crucible to give the K<sub>5</sub>In<sub>8</sub> shiny black powder. Then the K<sub>5</sub>In<sub>8</sub> powder was mixed with tellurium powder in the molecular ratio of 1 to 4 and heated at 550 °C for 4 h in a furnace. The resulting solid was dissolved in the water and filtered to remove the excess solid indium metal, while the ternary Zintl phase, K<sub>5</sub>InTe<sub>4</sub>, remained in solution. The percentage yield of K<sub>5</sub>InTe<sub>4</sub> was greater than 95%. The growth of single crystal of this Zintl phase from an aqueous solution has not been successful due to its extremely large solubility. Attempts to grow single crystals in liquid ammonia, ethylenediamine solution, or in the molten phase are in progress. Elemental analysis (Schwarzkopf Analytical Labs, NY) gave the following empirical formula: K<sub>4.92</sub>InTe<sub>3.83</sub>.

**Fe<sub>5</sub>(InTe<sub>4</sub>)<sub>2</sub>.** The ferrous indium telluride was prepared by the reaction of aqueous solutions of K<sub>5</sub>InTe<sub>4</sub> and FeCl<sub>2</sub>. In a typical preparation, while stirring the FeCl<sub>2</sub> solution (40 mL, 0.05 M), a stoichiometric quantity of the K<sub>5</sub>InTe<sub>4</sub> solution (50 mL, 0.1 M) was slowly added. A fine black precipitate was immediately formed, separated by suction filtration, washed with water and acetone, and dried overnight under vacuum. Elemental analysis (Schwarzkopf Analytical Labs, NY) gave the following empirical formula: Fe<sub>2.97</sub>InTe<sub>3.86</sub>. The analysis indicates that the material is slightly iron rich; however, previous analyses of transition metals in related alloys (e.g., M<sub>2</sub>SnTe<sub>4</sub><sup>11,12</sup>) commonly give higher apparent

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**Figure 1.** The dc magnetic susceptibility plotted as a function of temperature at a field of 0.5 kG (lower, zero field cooling; upper, field cooling) for 200-mg samples of  $\text{Fe}_5(\text{InTe}_4)_2$ .

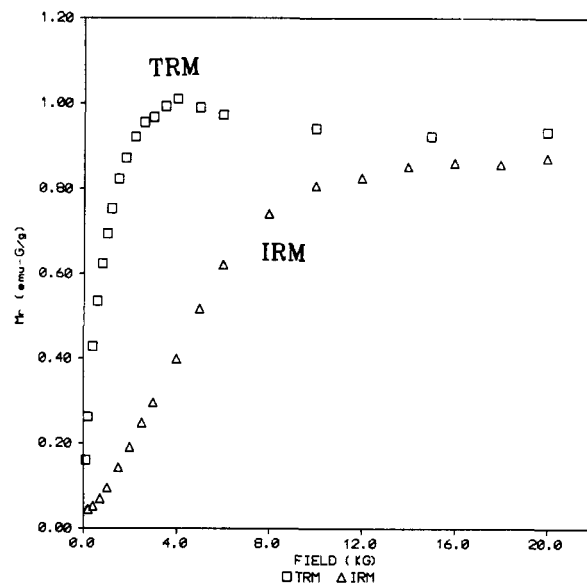
analysis values for the transition metal.

**Magnetism. Dc Magnetic Susceptibility.** The dc magnetic susceptibility and magnetization were conducted on a SHE Corp. VTS-50 superconducting SQUID susceptometer that is interfaced to the IBM 9000 computer system. Measurement and calibration techniques have been reported elsewhere.<sup>14</sup> Three types of experiments were conducted: dc magnetic susceptibility ( $M/H$ ), thermal remanent magnetization (TRM), and isothermal remanent magnetization (IRM), each as a function of field or temperature. The TRM experiment involves cooling the sample in an applied magnetic field and then measuring the remanent at zero magnetic field. The IRM experiment, on the other hand, involves cooling the sample in zero field, then applying a magnetic field, and finally measuring the remanent in zero magnetic field.

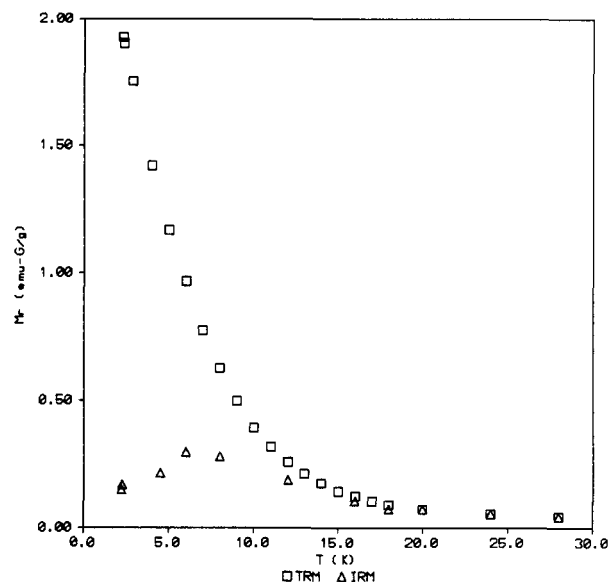
**Ac Magnetic Susceptibility.** The ac susceptibility was recorded on samples that were taken from the same synthetic batch used for the dc measurements. The data were recorded on a variable-frequency mutual inductance instrument. The operation and calibration of this instrument are described elsewhere.<sup>15</sup> Both the in-phase component  $\chi'$  and the out-of-phase component  $\chi''$  of the magnetic susceptibility at zero field were recorded at frequencies of 29 Hz, 282 Hz, and 1 kHz over the 4–100 K temperature region.

### Results and Discussion

At temperatures above 200 K, the inverse dc magnetic susceptibility of ferrous indium telluride falls on a straight line. A fit of the high-temperature magnetic data to the Curie-Weiss law [ $\chi = C/(T - \theta)$ ] results in a Curie constant  $C = 3.10$  emu K/mol, and the paramagnetic Curie temperature is found to be  $\theta = +80$  K. A Curie constant of 3.10 results in a  $g$  value of  $g = 2.04$  for iron(II) with  $S = 2$ . The large positive value of  $\theta$  indicates that ferromagnetic coupling between individual atomic moments occurs in this material. In Figure 1, the dc magnetic susceptibility is plotted for the temperature interval from 2 to 50 K. The zero-field cooling dc susceptibility rises to a maximum as the temperature is raised to 15 K and decreases upon further increase of the temperature. The magnetic field cooled dc susceptibility does not exhibit the same behavior in the measured temperature region. As the temperature is raised from the 2 K lower limit, the field cooling dc magnetic susceptibility decreases, albeit at a slower rate in the spin glass region. This behavior does not indicate normal ferromagnetic ordering at a temperature in accordance with the positive  $\theta$  of 80 K. On the contrary, the observed dc susceptibility of the zero-field cooled sample



**Figure 2.** Thermal remanent magnetization (square) and isothermal remanent magnetization (triangle) plotted as a function of magnetic field at a temperature of 6 K for  $\text{Fe}_5(\text{InTe}_4)_2$ .



**Figure 3.** Thermal remanent magnetization and isothermal remanent magnetization plotted as a function of temperature at a field of 3 kG for  $\text{Fe}_5(\text{InTe}_4)_2$ .

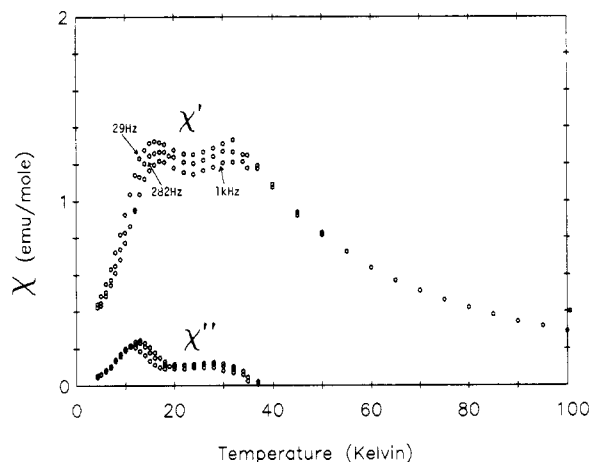
and of the field cooled sample suggest that this compound has a spin glass state with a freezing temperature of about 15 K; thus antiferromagnetic interactions are present as well.

Among the most diagnostic experiments for the characterization of the spin glass state is the analysis of the field dependence of the isothermal remanent magnetization (IRM) and thermal remanent magnetization (TRM). Both these magnetizations measured at 6.0 K for ferrous indium telluride have been illustrated on Figure 2. The hump at 4.0 kG in the TRM curve of this compound is characteristic of a spin glass state and has been observed in many systems.<sup>16</sup> For a spin-glass state at weak fields the TRM measurements give large remanences relative to the IRM, while at strong fields the IRM and TRM converge to the same saturation remanence. The effect seen for the TRM is greatly enhanced by performing the ex-

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**Figure 4.** In-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) components of the ac magnetic susceptibility plotted as a function of temperature at the frequencies indicated for  $\text{Fe}_5(\text{InTe}_4)_2$ .

periment at lower temperatures, whereas the IRM is little affected by the temperature. This is shown in Figure 3 where both TRM and IRM at an applied field of 3 kG are plotted as a function of temperature. The TRM and IRM curves merge near 15 K, the freezing point, which agrees with the susceptibility data at zero field cooling and field cooling.

There are some pronounced differences between the dc and ac magnetic susceptibility data. The in-phase magnetic susceptibility ( $\chi'$ ) and the out-of-phase magnetic susceptibility ( $\chi''$ ) are plotted together in Figure 4. The in-phase magnetic ac susceptibility ( $\chi'$ ) exhibits a broad maximum with two humps, one at approximately 32 K and the other near 15 K. The out-of-phase component ( $\chi''$ )

vanishes above 40 K, but at low temperatures two maxima in accordance with the behavior of  $\chi'$  are seen. The sharper peak in  $\chi''$  occurs at lower temperatures (ca. 15 K) and corresponds to the anomaly observed in the dc magnetic measurements. The change in the frequency of the ac experiment causes the anomalies to shift to slightly higher temperatures at higher frequencies. This effect is more pronounced at the anomaly around 15 K than at the anomaly at higher temperature. The higher temperature hump in the ac magnetic susceptibility data likely arises from short-range ferromagnetic ordering in accordance with the prediction from the high-temperature Curie-Weiss fits.

The behavior of the  $\chi'$  and  $\chi''$  data point to  $\text{Fe}_5(\text{InTe}_4)_2$  being an amorphous ferromagnetic material that begins to undergo extended short-range order around 35 K. This is consistent with the high-temperature Curie-Weiss fit of the dc magnetic data. At lower temperatures, a blocking of the domain wall migration sets in but is overruled by the spin-glass-like anomalies around 15 K. It is important to emphasize the dc data were measured in an applied magnetic field, while the ac data were measured at near zero field conditions. This could account for some of the apparent discrepancy between the ac and dc magnetic susceptibility data. A more detailed analysis of the present class of magnetic materials with special attention to the behavior of the magnetization as a function of field in the temperature region between 15 and 30 K will be reported in the near future.

**Acknowledgment.** C.J.O. acknowledges support from a grant from the Louisiana Education Quality Support Fund administered by the Board of Regents of the state of Louisiana and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

## Decomposition of Trimethylaluminum on Si(100)

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Received January 9, 1989

The mechanism of trimethylaluminum (TMAI) decomposition on a heated Si(100) substrate is studied by using temperature-programmed desorption, X-ray photoelectron spectroscopy, and electron energy loss spectroscopy. It is found that the TMAI adsorbs as dimers at low temperature. The dimers dissociate into monomers upon heating to 300–400 K. Further heating causes one of the methyl groups in the TMAI to react with a hydrogen on another methyl group, liberating methane. This leaves a  $\text{CH}_2$  group bound to the aluminum, which is seen clearly with EELS. Upon further heating, some of the remaining fragments undergo another intramolecular hydrogen shift, producing additional methane. The other fragments dissociate into aluminum atoms and  $\text{CH}_x$  groups. The  $\text{CH}_x$  groups are strongly bound on silicon. Hence, they decompose above 750 K, yielding adsorbed hydrogen and adsorbed carbon. The hydrogen desorbs between 750 and 850 K. The carbon remains bound to the silicon to high temperatures. These results show that carbon incorporation is an intrinsic part of the TMAI decomposition process on Si(100). Thus, TMAI would not be an appropriate source gas when one needs to produce films with very low carbon levels.

### Introduction

This paper is a continuation of previous work on the surface chemistry of molecules of interest for MOCVD and MOMBE.<sup>1,2</sup> The paper will focus on the mechanism of trimethylaluminum (TMAI) decomposition at low pressures on Si(100). Trimethylaluminum is an important

source gas for the growth of aluminum films on various substrates. It is also used as a source gas in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  growth by MOCVD. However, aluminum films grown with TMAI show high carbon levels and a columnar morphology.  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  films grown with TMAI often have high

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