FERRIMAGNETISM IN THE Ti-Sr-V-O SYSTEM

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We report here the observation of ferrimagnetism in a sample of nominal composition TiSrVO₄, prepared in a reducing atmosphere of 5% hydrogen in argon. The zero-field cooled magnetic moment (measured at applied field of 50 Oe) shows a net negative magnetic moment at temperatures below 30 K, rising to zero at a characteristic compensation temperature, Θc, of 30 K. The magnitude of the spontaneous magnetic moment reaches a maximum at T_max = 75 K, then decreases to a value close to zero at the Curie temperature, T_Curie, of 91 K. This behaviour is reminiscent of that observed previously in the field-cooled magnetic moment of the ferrimagnetic compound Co₂VO₄ measured at 700 Oe. (T_Curie = 158 K, T_max = 139 K and Θc = 70 K). Furthermore, the Ti-doped Sr-V-O system will inevitably be much more complex than the parent vanadium oxides and the Srⁿ⁺IVⁿO₃ⁿ⁺₁ system. Therefore, the Ti-doped Sr-V-O system will inevitably be much more complex than the parent vanadium oxides and the Srⁿ⁺IVⁿO₃ⁿ⁺₁ system.

From results obtained here from a number of samples prepared under our synthesis conditions, we have failed to obtain any evidence of superconductivity in the TiSrVO₄ compound from electrical resistivity measurements, which show a metal-to-metal transition at the Curie temperature.

I. INTRODUCTION

SINCE the announcement of the observation of superconductivity up to 130 K in the reduced Ti-Sr-V-O system by Matsuda et al. [2], many researchers have been motivated to work on this system. The confirmation of superconductivity at these temperatures would be of interest not only because of the enhanced Tc but also because it arises in a non-cuprate system. The V⁴⁺ ion present in the TiSrVO₄ system has a d¹ configuration which, in terms of hole formalism, is equivalent to Cu²⁺ (d⁹) and the observation of superconductivity in the vanadium system would aid greatly in understanding the mechanisms of superconductivity in the established copper-oxide systems. Moreover, vanadium oxides systems are known to exhibit a magnetic multiphasic (as evidenced by X-ray diffraction) and had a deep black colour. Resistance measurements revealed semiconducting behaviour. After regrinding and pelletizing (as described previously) of the melted sample, the pellets were then fired at 680°C under a 5% H₂ in Ar atmosphere for 5 hrs in an alumina boat, then cooled at a rate of 300°C/hr. The resulting samples were multiphasic (as evidenced by X-ray diffraction) and had a deep black colour.

Magnetic measurements were obtained by warming a zero-field cooled (ZFC) specimen in an applied magnetic field of 50 Oe, and monitoring the magnetic moment using a commercial SQUID magnetometer (Quantum Design MPMS1) modified with an enhanced controller, permitting very high temperature resolution (<0.1 K) measurements. This technique prevents temperature excursions in the sample, which can obliterately regions of the sample's cryomagnetic history. Standard four-point resistivity measurements were also carried out to investigate the electrical resistivity of the sample. Electrical contacts to the sample were made by fine copper wires with a conductive silver paint. The probe current was 1 mA. The temperature was recorded using a calibrated silicon diode sensor thermally bound to the sample.

II. EXPERIMENTAL

A sample of nominal composition TiSrVO₄ was prepared by mixing powders of Ti₂O₃, SrO₂ and V₂O₅ in appropriate proportions. The mixed powders were then pressed into a pellet 10 mm in diameter and 2 mm thick under an applied pressure of 5 tons/cm². The pellets were wrapped in gold foil (to prevent loss of thallium) and then placed in a tube furnace at 700°C for 3 hrs in a flowing oxygen atmosphere.

Subsequently, the sample was cooled to room temperature at a rate of 300°C/hr. After this treatment, the sample appeared completely melted with a pale-green color. Resistance measurements showed semiconducting behaviour. After regrinding and pelletizing (as described previously) of the melted sample, the pellets were then fired at 680°C under a 5% H₂ in Ar atmosphere for 5 hrs in an alumina boat, then cooled at a rate of 300°C/hr. The resulting samples were multiphasic (as evidenced by X-ray diffraction) and had a deep black colour.

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III. RESULTS AND DISCUSSION

In fig. 1 we show the temperature dependence of the zero-field cooled magnetization of the TiSrVO₄ sample, measured at applied field of 50 Oe. Interestingly, the material has a negative net magnetic moment below 30 K. On increasing the temperature, this moment becomes more positive, rising to zero at Θc = 30 K (defined here as the "compensation temperature"). Beyond Θc the spontaneous magnetic moment continues to rise rapidly with temperature, reaching a sharp maximum at T_max = 75 K before rapidly decreasing to a Curie temperature of T_Curie = 91 K. This behaviour is characteristic of all the samples we have prepared using the method described; it is also qualitatively similar to that...
observed in the field-cooled magnetization of the ferrimagnetic compound Co$_2$VO$_4$ measured at 700 Oe with $T_{\text{Curie}} = 158$ K, $T_{\text{m}}$, and $\Theta$ = 70 K [1] which is overlaid as shown in fig. 1 for comparison.

The explanation [1] for the cobalt vanadate behaviour is as follows: cobalt vanadate has an inverse spinel Co$_2$+[Co$_2$+V$^4$+]O$_4$ structure, in which the Co$^{2+}$ have different moments on the octahedral (B) and tetrahedral (A) sites. The strongest interaction, termed A-B, is between the Co$^{2+}$-O$^{2-}$-Co$^{2+}$ (A) and the V$^{4+}$ ions situated on the A sites. This gives a moment of V$^{4+}$ antiparallel to that of the Co$^{2+}$ ions on the B sites, and has a different temperature dependence. The variation of the relative magnitudes of these two effects with temperature gives rise to a compensation effect [1], which appears as a moment reversal. The ferrimagnetism arises from the fact that the magnitude of the magnetic moments on each of the two sublattices is not exactly equal. Thus when spontaneous antiparallel alignment occurs, the material, instead of having zero magnetic moment, has a net permanent magnetization.

[15] As may be seen in fig. 1, a strikingly similar ferrimagnetic behaviour can be seen in the zero-field cooled TISrVO$_4$ data. However, it is important to note that the field-cooled data (not shown here) for TISrVO$_4$ shows a very different behaviour; the moment rising rapidly from the Curie temperature to a saturation plateau at around 50 K of approximately three times the magnitude of the diamagnetic moment. This large and puzzling cryomagnetic hysteresis represents a very complicated magnetic behaviour for the Tl-Sr-V-O system, which the above theory can only partly explain. Isothermal M-H measurements of the TISrVO$_4$ sample for temperatures below 90 K ($T_{\text{Curie}}$), show a slow saturation followed by an almost linear increase in $M$ versus $H$ above 3 T, suggesting a ferrimagnetic coupling between the sublattice ions. Above 100 K, the M-H response tends quickly to paramagnetism. Similar measurements were made on samples of vanadium oxide, SrVO$_4$ compound and un reduced TISrVO$_4$, but all showed a simple Curie-Weiss type behavior.[16] We may thus rule out the possibility that ferrimagnetism in TISrVO$_4$ arises from any of these materials.

In fig. 2 we show the temperature dependence of the resistivity of the TISrVO$_4$ sample. The resistivity decreases from $1.3 \times 10^{-3}$ to $1.25 \times 10^{-5}$ cm over the range 295 K to 7 K. Here it begins to flatten out, but at no point does it fall to zero. It is important to note the distinct change in slope around the Curie temperature: the slope of the resistivity from 295 K to 100 K is smaller than that from 90 K to 20 K (i.e. the material is more metallic between 90 K and 20 K than it is above 100 K.) This corresponds to a metal-to-metal transition at the Curie temperature, and indicates that the spin-induced scattering of the conduction electrons makes a significant contribution to the resistivity above the Curie temperature.

More detailed studies of the crystal structure of the Tl-Sr-V-O compound and its correlation to the observed ferrimagnetism are presently underway.

**References**

16. R.S. Liu et al., unpublished.