Magnetic property of layered compound $NbFeTe_2$

Jian H. Zhang
Department of Chemistry, Xavier University of Louisiana, New Orleans, Louisiana 70125

Feng Chen
Department of Chemistry, Rider University, Lawrenceville, New Jersey 08648

Jing Li
Department of Chemistry, Rutgers University, Camden, New Jersey 08102

Charles J. O'Connor
Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

$NbFeTe_2$ is a layered cluster compound in which intra Fe–Fe bond distance is 2.488 Å. The magnetic susceptibilities between 100 and 300 K are fit to Curie–Weiss law with $C=1.29$ emu K/mol, and $\theta=+69.2$ K. The effective magnetic moment of 3.67 μ_B per Fe at 300 K corresponding to three unpaired electrons may suggest the formation of Fe–Fe single bond. Mössbauer spectrum at 77 K shows a paramagnetic doublet with $\delta=0.36$ mm/s and $\Delta E=0.62$ mm/s. The χ_{ac} measurement reveals the occurrence of a spin glass transition at $T_f=44.0$ K. The irreversibility of magnetic properties below T_f has been studied with the measurements of the dc susceptibility, remanent magnetization, and hysteresis loop for both zero field cooled and field cooled samples. The competition between antiferromagnetic and ferromagnetic interactions probably cause the spin glass behavior. © *1997 American Institute of Physics.*[S0021-8979(97)34008-0]

I. INTRODUCTION

Niobium and tantalum chalcogenides with low-dimensional structures frequently display interesting physical properties such as superconductivity,[1] charge density waves,[2] and metal-insulator transition,[3] as well as intercalation chemistry.[4] Therefore, their properties and structural chemistry have attracted considerable interest. Recently, a family of ternary niobiun and tantalum tellurides with general formulas $MNbTe_2$ and $MTaTe_2$, where M=Fe, Co, and Ni, has been synthesized and characterized.[5,6] All of them crystallize in layered structures, although the stacking of layers in each compound is different.

The crystal structure of $NbFeTe_2$, determined with single crystal x-ray diffraction (XRD) method[5] by one of the authors, is orthorhombic. Its layered framework structure consists of a plane of distorted honeycombs Nb(Nb–Nb =3.187–3.213 Å), with pairs of Fe atoms (Fe–Fe=2.488 Å) sitting at the center of every Nb hexagon. The metal layers are capped above and below by Te atoms, leading to a distorted tetrahedral coordination for Fe and a pseudooctahedral coordination for Nb. The previous study did not give insight into the complex magnetic interaction at low temperatures. To better understand the electronic structure and magnetic interaction in this compound, we have performed the detailed magnetic studies using both ac and dc techniques.

II. EXPERIMENTAL WORK

Polycrystalline samples of $NbFeTe_2$ were prepared with a previously described method.[5] The samples were characterized by XRD using a Rigaku D/Max horizontal scan diffractomater. The XRD patterns of the samples were consistent with the powder diffraction pattern calculated from the single crystal data with the computer program DISPOW. By comparing the XRD pattern of the samples with those of known phases containing Fe in JCPD database, it was confirmed no magnetic impurity phases present in these samples. The average particle size of the samples was estimated to be greater than 0.1 μm using the Warren's method.[7] Mössbauer spectra, determined in a time mode using a conventional constant-acceleration spectrometer, also confirmed no ordered background impurities.

Magnetic measurements were performed on a quantum design MPMS-5S SQUID susceptimeter. The temperature dependence of $\chi_{dc}(=M/H)$ was determined at a certain fixed field using the temperature cycling, following the usual zero-field cooling (ZFC) and field cooling (FC) procedures. In the $\chi_{ac}(=dM/dH)$ measurement, a magnetic field of 1.0 Oe was oscillated at a desired frequency under a static zero field while the temperature was scanned from 6.0 to 80 K. The remanent magnetization and the hysteresis loops for both ZFC and FC samples were measured. In the thermal remanent magnetization (TRM) measurement, the sample was slowly cooled in an applied field to temperatures below the spin glass freezing point, then the field was switched off, and the remanent magnetization was measured after a specified elapsed time of 300 s. In the isothermal remanent magnetization (IRM) measurement, on the other hand, the sample was slowly cooled in a zero field to temperatures below the spin glass freezing point, exposed to an applied field for a certain time (300 s), and then the applied field was quenched and the remanent magnetization was measured after 300 s.

III. RESULTS AND DISCUSSION

The magnetic data of $FeNbTe_2$ in the high temperature region follow Curie–Weiss behavior. A least-squares fitting of the molar susceptibility between 100 and 300 K to the Curie–Weiss expression, $\chi=C/(T-\theta)$, gives that $C=1.29$ emu K/mol and $\theta=+69.2$ K. The calculated effective magnetic moment at 300 K is only 3.67 μ_B/Fe atom. This value is significantly lower than those expected for a high spin

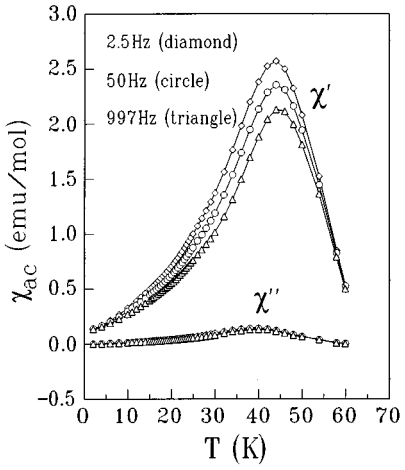

FIG. 1. Plot of χ_{ac} vs T at various frequencies. $H_{ac}=1$ Oe, $H_{dc}=0$. The solid lines are guides to eye only.

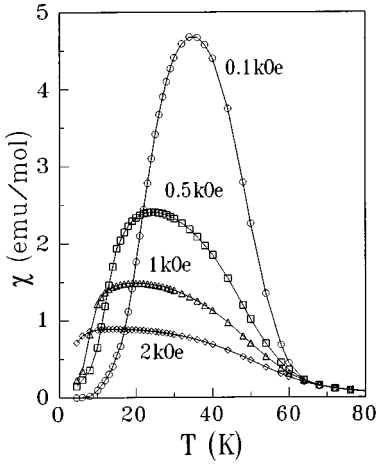

FIG. 3. Plot of χ_{dc} vs T for a FC sample at various measuring fields. The solid lines are guides to eye only.

Fe(III) ($\mu_{eff}=5.9\ \mu_B$), or a high spin Fe(II) ($\mu_{eff}=4.9\ \mu_B$). The effective moment of 3.67 μ_B corresponding to three unpaired electrons may suggest the formation of Fe–Fe single bond, supported by the short Fe–Fe distance of 2.488 Å, which is comparable to 2.482 Å in metal iron.[8] The large and positive θ value indicates the existence of a strong ferromagnetic coupling between the two effective $S=3/2$ centers through the bridging Te atoms.

In the previous article, Li *et al.* have assigned the oxidation state of +2 to Fe, since Fe(III) would leave the very electropositive Nb at a low oxidation state of +1, which is very unlikely in a telluride.[6] Mossbauer spectra of $FeNbTe_2$ have been obtained to assist in the determination of the oxidation state and spin state of Fe. Mossbauer spectrum at 77 K exhibits a well defined paramagnetic doublet with the isomer shift of 0.36 mm/s and the quadrupole splitting of 0.62 mm/s. Reiff has suggested[9] that Mossbauer isomer shifts of 0.60 and about 0.20 mm/s can be considered diagnostic values for high spin Fe(II) and high spin Fe(III) tetrahedrally coordinated to sulfur, respectively, according to his investigation of a series of Ba–Fe–S phases. The relatively small isomer shifts result from the electron delocalization of irons to liqands in highly covalent sulfides. The covalent bonding is even stronger in tellurides than in sulfides. As a result, the smaller isomer shifts for Fe(II) tetrahedrally coordinated to Te is not unreasonable due to stronger electron delocalization. The strong direct antiferromagnetic coupling in Fe–Fe bond may result in the decrease in the isomer shift as well.

At low temperatures, $FeNbTe_2$ exhibits a complex magnetic behavior. Figure 1 shows the temperature dependence of χ_{ac} at various frequencies. The cusps in χ'_{ac} and χ''_{ac} curves are characteristic of a spin glass state, and are due to the inability of the frozen spins response to the alternating magnetic field. The spin glass freezing temperature (T_f) is determined to be 44.0 K and slightly frequency dependent. Temperature-dependent χ_{dc} data obtained for the ZFC and FC samples are shown in Fig. 2. At low temperatures, the ZFC and FC magnetizations significantly diverge. The FC curve reaches a plateau, while the ZFC curve shows a dramatic decrease in magnetization as seen in many typical spin glass systems. The maximum in the ZFC curve characteristic of a spin glass state is strongly field dependent as shown in Fig. 3, which may be due to the existence of strong short range ferromagnetic ordering in this compound.

A striking phenomenon in spin glasses is the observation of irreversible behavior in the temperature region of the spin glass freezing transition at lower temperatures. One of the

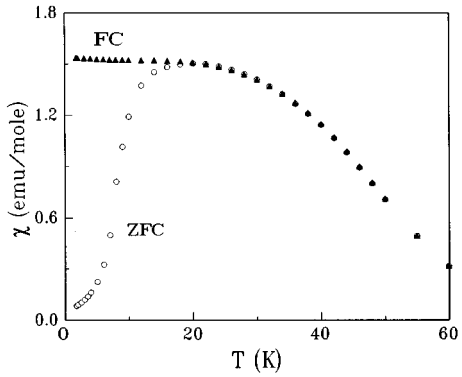

FIG. 2. Plot of χ_{dc} vs T as determined at 1.0 kOe.

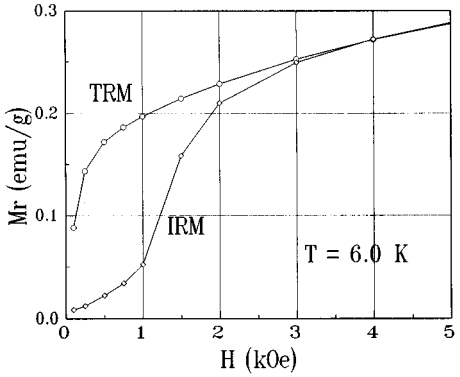

FIG. 4. Plot of remanent magnetization vs field at 6.0 K. The solid lines are guides to eye only.

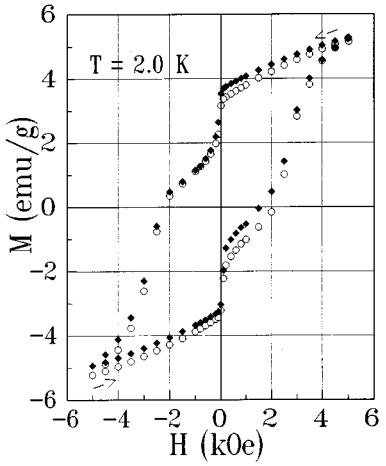

FIG. 5. Plot of hysteresis loops at 2.0 K for a ZFC sample (open circle), and the FC sample in a field of 5 kOe (filled triangle).

frequently performed diagnostic experiments for the study of irreversible effect of a spin glass state is the analysis of the field dependence of TRM and IRM. The TRM and IRM experiment for $FeNbTe_2$ at 6.0 K is illustrated in Fig. 4. The general features for this system are consistent with the observation for other well documented spin glass systems, i.e., the field dependence of TRM is linear at small fields, while the field dependence of IRM seems rather to be quadratic. At high fields, both tend to the same saturation value, since the irreversible effects are negligible for fields exceeding the critical field where TRM and IRM merge. However, the characteristic hump always seen in the field dependence of TRM for other spin glasses is not observed in this system.

A spin glass state shows hysteresis phenomena as in ferromagnets at temperatures below T_f due to irreversibility if the applied field is cycled from positive to negative values and back. Figure 5 shows the hysteresis loops measured at 2.0 K for both ZFC and FC samples. The ZFC sample exhibits a hysteresis loop with a large coercive field of 4200 Oe which is antisymmetric around the origin. The shape of the loop is unusual. In the small fields after the reversal of the direction of the field, the magnetization has a dramatic change. The similar behavior has been observed in a planar antiferromagnet[10] where intralayer and interlayer magnetic interactions are different. Thus, the observed shape of the loop may be associated with the layered structure of $FeNbTe_2$ as well as the anisotropic property of Fe. The hysteresis loop for the FC sample remains the same shape, but is slightly displaced due to the presence of small unidirectional exchange interaction in the sample.

$FeNbTe_2$ is a stoichiometric and crystalline compound that exhibits semiconductivity as indicated by a negative coefficient of $d\rho/dT^3$. The conduction electron mediated RKKY interaction may not be used to explain the origin of the spin glass state in this compound in which there are no site disorder and/or bond disorder as existed in transition metal alloys and amorphous magnetic alloys. Our magnetic measurements have confirmed that there exist direct antiferromagnetic interactions within iron clusters, and ferromagnetic interactions between iron clusters through Te covalent network. The frustration that arises from the competing interactions between nearest neighbors (antiferromagnetic) and next nearest neighbors (ferromagnetic) probably causes the spin glass transition at 44.0 K.

ACKNOWLEDGMENT

J.H.Z. would like to acknowledge the support by a Cottrell College Science Award of Research Corporation.

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