Temperature dependence of magnetic anisotropy constant in iron chalcogenide Fe_3Se_4: Excellent agreement with theories

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Magnetic hysteresis loops were measured for ferrimagnetic iron chalcogenide Fe_3Se_4 nanoparticles in the whole temperature range below the Curie temperature T_C (315 K). The coercivity of the material is huge, reaching about 40 kOe at 10 K. The magnetic anisotropy constant K was determined from the magnetic hysteresis loop using the law of approach to saturation. The deduced anisotropy constant at 10 K is 5.22×10^6 erg/cm^3, which is over one order of magnitude larger than that of Fe_3O_4. We also demonstrated that the experimental magnetic hysteresis loop is in good agreement with the theoretical curve calculated by Stoner and Wohlfarth for a noninteracting randomly oriented uniaxial single-domain particle system. Moreover, we show that K is proportional to the cube of the saturation magnetization M_s, which confirms earlier theoretical models for uniaxial magnets. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4759352]

I. INTRODUCTION

Iron chalcogenide compounds were studied quite extensively[1–4] during 1950s and 1960s. Among them, Fe_3Se_4 and Fe_7Se_8 are ferrimagnetic with Curie temperatures of 314 K and 450 K, respectively. Recently, superconductivity has been discovered[5] in the tetragonal PbO-type $\alpha-FeSe_{2-x}$. The observation of ferrimagnetism or superconductivity in iron chalcogenide compounds implies that superconductivity can occur in the vicinity of a magnetic instability. This may help understand high-temperature superconductivity in cuprates and iron pnictides where superconductivity occurs in the proximity of antiferromagnetic instability. Recent magnetic data of ferrimagnetic Fe_3Se_4 nanostructures have demonstrated that the coercivity values in Fe_3Se_4 nanoparticles are giant, reaching about 40 kOe at 10 K and 4 kOe at room temperature.[6] Because of the giant coercivity, this iron chalcogenide compound may have broad applications ranging from high-density data storage media to permanent magnets.

From fundamental point of view, Fe_3Se_4 should also be an interesting compound because it is a uniaxial magnet with huge magnetic anisotropy.[6] Theoretically, it was shown that the temperature dependencies of the magnetic anisotropy constant K in uniaxial and multiaxial ferromagnets differ significantly.[7,8] The dependencies are also influenced by the degree of correlation between the directions of adjacent spins. The theories of Van Vleck[7] and Zener[8] can be considered as the limiting cases of no correlation and complete correlation, respectively. These theories yield a relation between $K(T)$ and $M_s(T)$ as

$$K(T)/K(0) = [M_s(T)/M_s(0)]^n, \quad (1)$$

where M_s is the saturation magnetization and n is an exponent depending on correlation and crystal symmetry.[7,8] In the case of no correlation, n was calculated[7] to be 3 and 6 for hexagonal (uniaxial) and cubic (multiaxial) crystals, respectively. In the case of complete correlation, the exponent n increases from 6 to 10 for cubic crystals while n remains 3 for hexagonal crystals.[8] Therefore, the theoretical value of n is 3 for uniaxial magnets independent of correlation. The above theoretical predictions were confirmed by the experimental results for Fe and Ni with cubic symmetry.[8] But for uniaxial magnets, the experimental value of n is between 1.0 (Ref. 10) and 2.7 (Ref. 9), which appears inconsistent with the theories.[7,8]

Here, we report magnetic hysteresis loops for ferrimagnetic iron chalcogenide Fe_3Se_4 nanoparticles (about 30 nm). The coercivity of the nanoparticles reaches about 40 kOe at 10 K. The magnetic anisotropy constant K was precisely determined from the magnetic hysteresis loop using the law of approach to saturation (LAS). The anisotropy constant at 10 K is 5.22×10^6 erg/cm^3. Moreover, K was found to be proportional to the cube of M_s in the whole temperature range below the Curie temperature T_C (315 K). This temperature dependence confirms the earlier theories of Van Vleck[7] and Zener.[8]

II. SAMPLE PREPARATION

Fe_3Se_4 nanoparticles were synthesized by the organic-solution-phase chemical decomposition method.[6] In a typical reaction, the mixture of $Fe(acac)_3$ (1.5 mmol) and Se powders (2 mmol) was added in 15 ml of oleylamine in a flask. Under inert gas atmosphere flow, the mixture was heated to 120 °C. The solution was kept at this temperature for 60 min to remove low boiling point solvents and oxygen. Then, the temperature was raised to 310 °C and kept at 310°C for 1 h. The solution was cooled to room temperature. The Fe_3Se_4 nanoparticles were precipitated by adding 20 ml of 2-propanol and centrifuged at 8000 rpm for 10 min.

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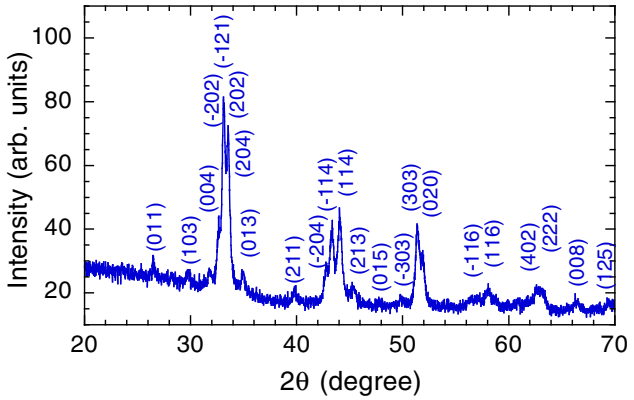

FIG. 1. XRD spectrum for Fe_3Se_4 nanoparticles.

III. RESULTS

Figure 1 shows x-ray diffraction (XRD) spectrum of our Fe_3Se_4 nanoparticles. The XRD spectrum can be indexed by the standard Fe_3Se_4 phase with the lattice constants: $a = 6.205(12)$ Å, $b = 3.524(7)$ Å, and $c = 11.262(18)$ Å, in excellent agreement with the reported values.[9] There are no impurity phases within the XRD resolution. From the width of the XRD (011) and (103) peaks and using Scherrer's formula, we estimated the mean particle diameter to be about 28 nm, close to that (32 nm) for a similarly prepared sample.[6]

Figure 2(a) shows temperature dependence of the magnetization for Fe_3Se_4 nanoparticles, which is measured in a magnetic field of 1.0 kOe. Magnetic moment was measured using a Quantum Design vibrating sample magnetometer (VSM) with a resolution better than 1×10^{-6} emu. There is a small thermal lag (about 6 K) between heating and cooling measurements. The Curie temperature (corresponding to the inflection point of the magnetization curve) is 315 K. In Fig. 2(b), we plot magnetic hysteresis loops for the sample at 10 K and 300 K, respectively. The data shown have been thinned for clarity. At 300 K, the magnetization increases almost linearly with magnetic fields in the field range of larger than 20 kOe. This quasilinear contribution should arise from superparamagnetism of some ultrafine particles. The best fit (solid line) to the data at 300 K in the high-field range (>20 kOe) by an equation: $M_s + A[\coth(\mu H/k_BT) - k_BT/\mu H]$, yields a saturation magnetization M_s of 1.893 ± 0.002 emu/g, $A = 4.1 \pm 0.1$ emu/g, and $\mu = 85.5 \pm 0.5 \mu_B$. Here, $[\coth(x) - 1/x]$ is the Langevin function, μ is the total moment of an ultrafine particle, and μ_B is the Bohr magneton. The values of μ and A imply that the mean diameter of the ultrafine particles is 3.45 nm and that the sample contains about 30% of the ultrafine particles. These particles are too fine to be resolved in the XRD spectrum. The ratio of the remanent magnetization M_r and saturation magnetization M_s is found to be 0.49. At 10 K, the magnetization is not saturated even in the highest reachable field (90 kOe) due to a very large coercive field H_C of 37.2 kOe. Magnetic hysteresis loops were also measured at other temperatures such as 50 K, 100 K, 150 K, 200 K, and 250 K, but we only display typical data at 10 K and 300 K for clarity. From the hysteresis loop at each temperature, we can directly determine the remanent magnetization M_r and coercive field H_C. Fig. 3 shows

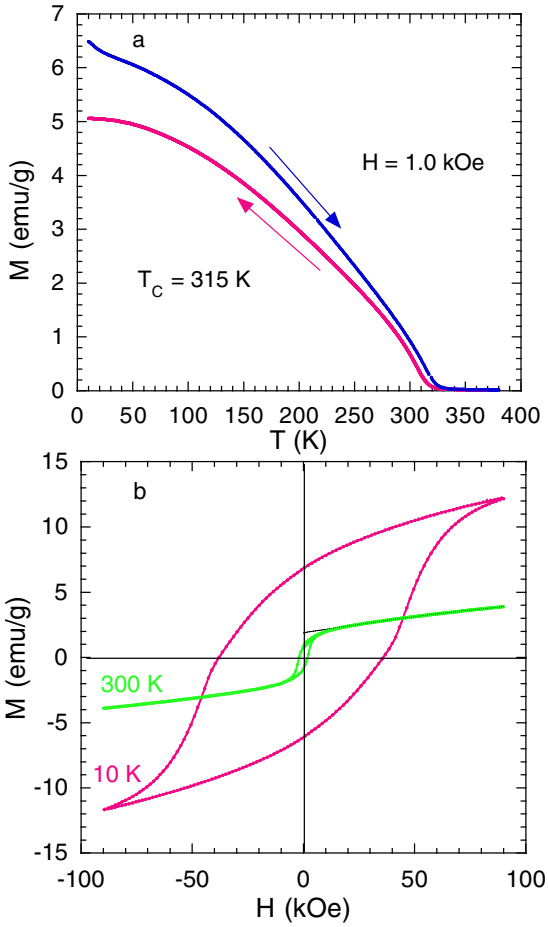

FIG. 2. (a) Temperature dependence of the magnetization for Fe_3Se_4 nanoparticles. The Curie temperature (corresponding to the inflection point of the magnetization curve) is 315 K. (b) Magnetic hysteresis loops of Fe_3Se_4 nanoparticles at 10 K and 300 K, respectively. The coercive field H_C at 10 K is 37.2 kOe and reduced to 1.94 kOe at 300 K. The best fit (solid line) to the data at 300 K in the high-field range (>20 kOe) by an equation: $M_s + A[\coth(\mu H/k_BT) - k_BT/\mu H]$ yields a saturation magnetization M_s of 1.893 ± 0.002 emu/g and $\mu = 85.5 \pm 0.5 \mu_B$.

temperature dependencies of M_r and H_C. As expected, both M_r and H_C decrease with increasing temperature. The temperature dependence of M_r can be fitted by an equation: $M_r(T) = M_r(0)[1 - (T/T_0)^p]$ with three fitting parameters: $M_r(0)$, p, and T_0 (a characteristic temperature). The best fit yields $M_r(0) = 6.27 \pm 0.07$ emu/g, $p = 2.1 \pm 0.1$ and $T_0 = 322 \pm 3$ K.

It is well known that the saturation magnetization M_s for bulk magnetic systems follows Bloch's law[11] of the form $M_s(T) = M_s(0)[1 - (T/T_0)^p]$ with $p = 1.5$. However, the temperature dependence of M_s for magnetic nanoparticles will deviate from Bloch's law due to finite-size effect.[12,13] A modified Bloch's law with p close to 2 is expected for magnetic nanoparticles.[12,13] The exponent $p = 2.1$ found for $M_r(T)$ suggests that $M_r(T)$ in our magnetic nanoparticle system should have a similar function form as $M_s(T)$. This simple proportionality between $M_r(T)$ and $M_s(T)$ could occur if our nanoparticle assembly is a noninteracting single-domain particle system. In 1948, Stoner and Wohlfarth (SW)[14] predicted zero-temperature magnetic hysteresis loop for noninteracting randomly oriented uniaxial single-domain particle

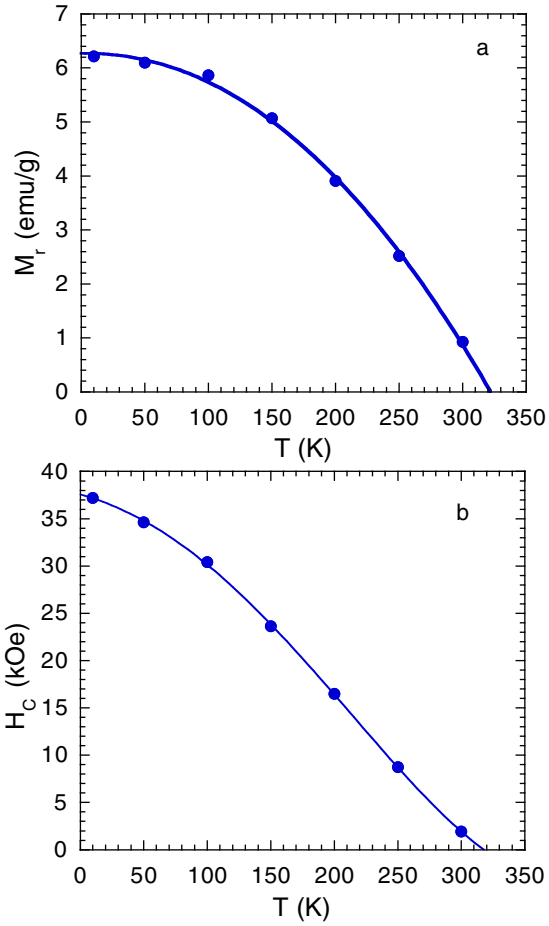

FIG. 3. (a) Temperature dependence of M_r for Fe_3Se_4 nanoparticles. M_r data can be fitted by an equation: $M_r(T) = M_r(0)[1 - (T/T_0)^p]$ with $p = 2.1 \pm 01$. (b) Temperature dependence of H_C for Fe_3Se_4 nanoparticles.

systems. One of essential features is that $M_r/M_s = 0.5$. Extension of the SW theory to finite temperatures and multiaxial particle system showed that the ratio M_r/M_s is independent of temperature.[15] This implies a simple proportionality between $M_r(T)$ and $M_s(T)$. Therefore, our $M_r(T)$ data may imply that our Fe_3Se_4 nanoparticle assembly should behave like a noninteracting randomly oriented uniaxial single-domain particle system with $M_r(T)/M_s(T) = 0.5$. This is justified from the data at 300 K (see Fig. 2(b) above) and the data at 10 K (see the analysis in Fig. 5 below).

The intrinsic magnetic parameters can be deduced from quantitative analyses of the isothermal $M(H)$ curves by using the LAS. In the case of uniaxial magnets, the LAS can be written as,[16,17]

$$|M(T,H)| = M_s(T)\left[1 - \frac{H_K^2(T)}{15H^2}\right] + |H|\chi(T), \qquad (2)$$

where the anisotropic field $H_K(T)$ is given by

$$H_K(T) = 2K(T)/M_s(T), \qquad (3)$$

and $\chi(T)$ is the paramagnetic susceptibility due to the presence of paramagnetic impurity phases and/or to superparamagnetism of some ultrafine particles.

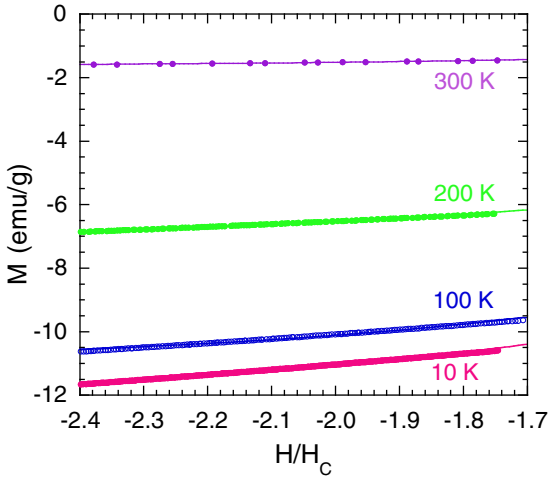

FIG. 4. The isothermal $M(H)$ curves in the third quadrant in the field range: $17H_C(T) \le |H| \le 24H_C(T)$. The solid lines are fitted curves with Eq. (2).

We fit the $M(H)$ curves in the negative field branch by Eq. (2) in the field range: $1.7H_C(T) \le |H| \le 2.4H_C(T)$. At 10 K, the field range corresponds to 65 kOe $\le |H| \le$ 90 kOe. The fit to the data in this field range ensures an excellent fitting quality with the R-squared parameter larger than 0.990. In order to obtain a reliable H_K value at each temperature, the field range for fitting should be scaled with $H_C(T)$. The solid lines in Fig. 4 are the best fitted curves of Eq. (2) with two fitting parameters: $H_K(T)$ and $\chi(T)$ and one fixed parameter $M_s(T) = 2M_r(T)$ (see above discussion and Fig. 5 below). At each temperature, the fitting quality is excellent; the R-squared parameter remains close to 0.990. The uncertainty of $H_K(T)$ is small (<0.9%). The fitting parameter H_K at 10 K is 104.5±0.2 kOe, which is similar to that ($\simeq 2H_C = 80$ kOe) reported in Ref. 9.

In order to justify our fitting procedure, we compare the magnetic hysteresis loop at 10 K with the theoretical curve predicted from the SW theory. The solid line in Fig. 5 is the SW theoretical curve with $H_K = 105$ kOe and $M_s = 2M_r = 13.20$ emu/g. Here, $M_r = 6.60$ emu/g is the

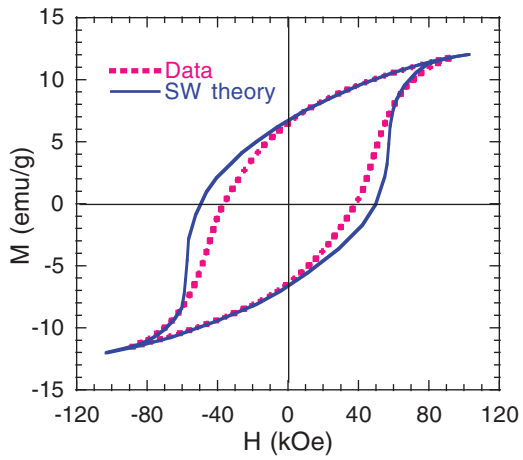

FIG. 5. Experimental magnetic hysteresis loop of Fe_3Se_4 nanoparticles at 10 K (dotted line) and the SW theoretical curve calculated for a noninteracting randomly oriented uniaxial single-domain particle system (solid line). The theoretical curve is obtained by rescaling the original normalized curve[14] with $H_K = 105$ kOe and $M_s = 2M_r = 13.20$ emu/g.

remanent magnetization in the positive M direction, which is slightly larger than that (6.22 emu/g) in the negative M direction. The reason for the small difference is unclear. The data shown in Fig. 5 have been subtracted by $H\chi(T)$, the paramagnetic contribution obtained from the best fit above. It is striking that the agreement between the data and theoretical curve is excellent except for H around H_C. This excellent agreement further justifies our fitting procedure where we have assumed that $M_s(T) = 2M_r(T)$. Experimental value of H_C is lower by about 25% compared with the SW theoretical prediction for a noninteracting randomly oriented uniaxial single-domain particle system. The mean particle size of about 30 nm for our sample should be small enough for them to be classified as single-domain particles. Since these particles are closely packed during the magnetic measurements, the reduced H_C is possibly caused by finite magnetic interactions among the magnetic particles. If this speculation is relevant, coating Fe_3Se_4 nanoparticles with amorphous silica may increase the H_C values because coating magnetic nanoparticles with amorphous silica has been shown to reduce interparticle interactions effectively.[18,19]

The magnetic anisotropy constant K can be calculated using $K(T) = H_K(T)M_s(T)/2 = H_K(T)M_r(T)$. From the fitting parameter $H_K(T)$ and the $M_r(T)$ data, we calculate the magnetic anisotropy constant $K(T)$. The result is shown in Fig. 6(a). At 10 K, the anisotropy constant is 5.22×10^6 erg/cm^3, which is over one order of magnitude larger than that of Fe_3O_4 (Ref. 20). This difference most likely originates from the orthorhombic structure of Fe_3Se_4, which has a crystal field with a lower symmetry than that of cubic spinel structured Fe_3O_4. It is worth noting that our deduced K value is about half of the value (1.1×10^7 erg/cm^3) reported in Ref. 9. Because both H_K and M_s reported in Ref. 9 are similar to those reported here, the discrepancy does not arise from the data difference but from a calculation mistake in Ref. 9. Our experimental value of K is about 40% of the theoretical value (1.2×10^7 erg/cm^3) calculated using the projector augmented-wave (PAW) method.[9] This big difference implies inaccuracy of the PAW method and an improved theoretical work is required to yield better agreement between the experimental and theoretical values.

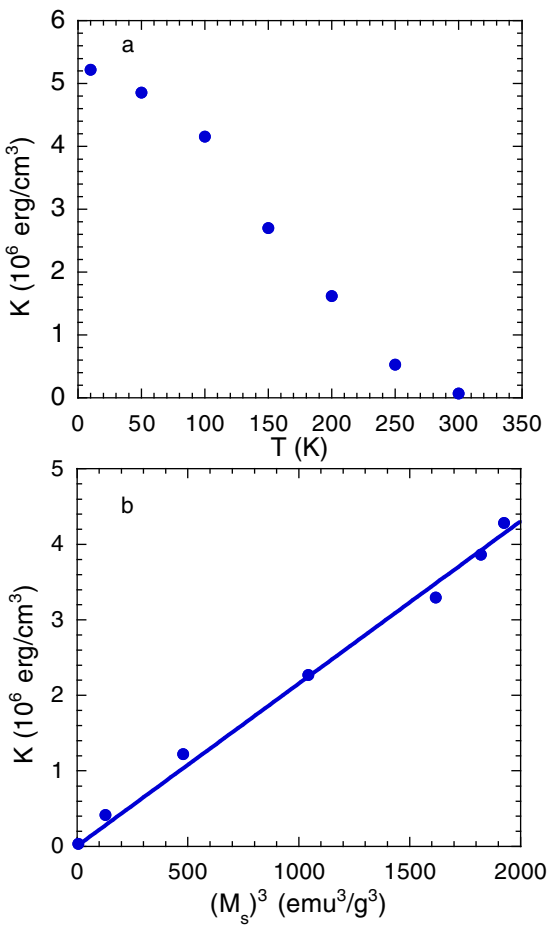

FIG. 6. (a) Temperature dependence of magnetic anisotropy constant K. (b) Plot of K versus M_s^3. K is linearly proportional to M_s^3 in the whole temperature range below T_C. This is consistent with Eq. (1) with $n = 3.0$.

In Figure 6(b), we show the plot of K versus M_s^3. It is apparent that K is linearly proportional to M_s^3 in the whole temperature range below T_C. This is consistent with Eq. (1) with $n = 3.0$. Thus, our current data clearly confirm the theoretical predictions for uniaxial magnets.[7,8]

IV. CONCLUSION

In summary, we have quantitatively analyzed magnetic hysteresis loops measured for ferrimagnetic iron chalcogenide Fe_3Se_4 nanoparticles. The magnetic hysteresis loops clearly show giant coercivity values, reaching about 40 kOe at 10 K. We have determined the magnetic anisotropy constant K from the magnetic hysteresis loop using the law of approach to saturation. The deduced anisotropy constant at 10 K is 5.22×10^6 erg/cm^3, which is over one order of magnitude larger than that of Fe_3O_4. We also show that the measured magnetic hysteresis loop is in good agreement with the theoretical prediction of Stoner and Wohlfarth for a noninteracting randomly oriented uniaxial single-domain particle system. Moreover, we have found that K is proportional to the cube of the saturation magnetization M_s. This temperature dependence is in excellent agreement with the earlier theoretical models for uniaxial magnets.

ACKNOWLEDGMENTS

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