Quantum Size Effects on Vanadium Nanoparticles

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Vanadium nanoparticles of two sizes were fabricated by pulse laser deposition. Transmission electron microscopy (TEM) images revealed that the diameters of the particles two samples were 2.5 and 4 nm. X-ray diffraction was used to determine the purity and lattice constant. Both samples were in the cubic 1–3-m phase. The lattice constants increased with diameter: the 4- and 2.5-nm samples had constants that were 0.42% and 0.55% larger than the lattice constant of the bulk, respectively. Superconductivity behaviors were determined by experiments on magnetic susceptibility. No Meissner effect was observed in the 2.5-nm nanoparticles. The T_c of the 4-nm nanoparticles was about 5.4 K, and accompanied a H_c of about 500 Oe. The critical diameter of vanadium nanoparticles for superconductivity can be estimated using Kubo theory[1,2]. The calculated critical diameter of the Kubo gap for superconductivity (∼1.6 meV) is about 3 nm. This fact is believed to be the main explanation of the lack of superconductivity in 2.5-nm nanoparticles.

***Index Terms*—Critical diameter, Kubo gap, nano, superconductivity.**

I. Introduction

BOTH electronic and lattice properties can differ between bulk material and nanometer-sized pieces of materials. The disruption of lattice periodicity at the surface of a particle and the reduction of the mean free path of carriers by spatial limitations are known as small size effects. Clearly, the discrete electron levels that are associated with quantum confinement may become significant. The most noticeable small size effect is the loss of superconductivity, which occurs when the electron level separation near the Fermi level is separated from it by an energy that is closely becoming comparable to the Bardeen–Cooper–Schrieffer (BCS) superconducting gap [1]–[3]. This criterion, known as the Anderson criterion, is usually satisfied when particles are only a few nanometers in size [4]–[6]. Kubo first proposed his famous function that specified energy required to remove an electron from the surface of a small metal particle. Halperin derived a complete formula to describe single electron level spacing for simple metal system [7]. Today, these can be utilized to predict superconductivity in the particle of a particular element and size.

II. Experiments

Two sets of vanadium nanoparticles were fabricated by pulse laser deposition. A 200-mW pulse laser beam was guided to, and incident on, the surface of a pure vanadium rod with a frequency of 20 Hz. Each pulse produced nanoparticles and spread out in the argon-filled chamber, collected by a spin coater with liquid nitrogen cooling. X-ray diffraction and transmission electron microscopy (TEM) were used to characterize the samples. Structural refinements were made for all samples using the Generalized Structure Analysis System (GSAS) program [8]. Magnetic susceptibilities were determined between 2 and 300 K using a commercial Quantum Design magnetometer [physical property measurement system (PPMS)] with both alternating current (ac) and direct current (dc) experimental setups.

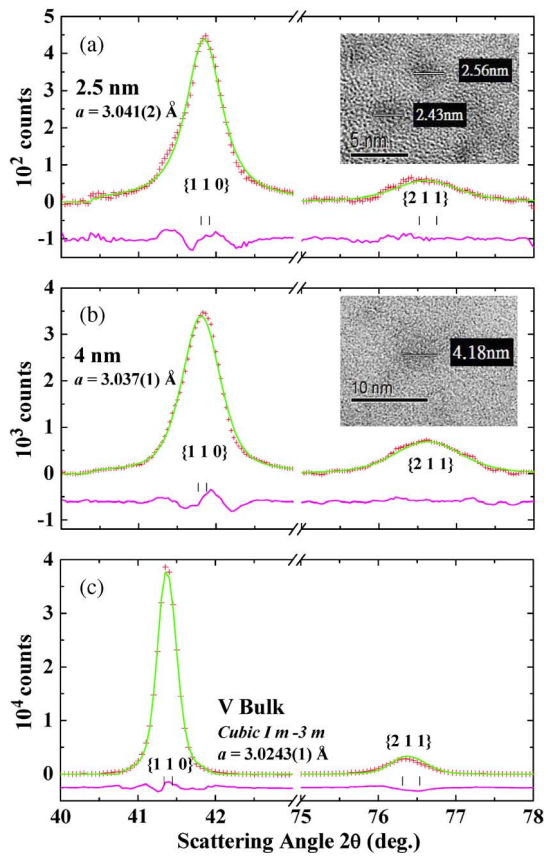

Fig. 1. Rietveld refined X-ray diffraction patterns of (a) 2.5 nm, (b) 4 nm, and (c) bulk vanadium. Insets display TEM images of corresponding diffraction patterns.

III. Result and Discussion

The diameters of the particles were determined from TEM images, which are shown in the insets in Fig. 1(a) and (b). Two different samples with average particle sizes of 2.5 ± 1 nm and

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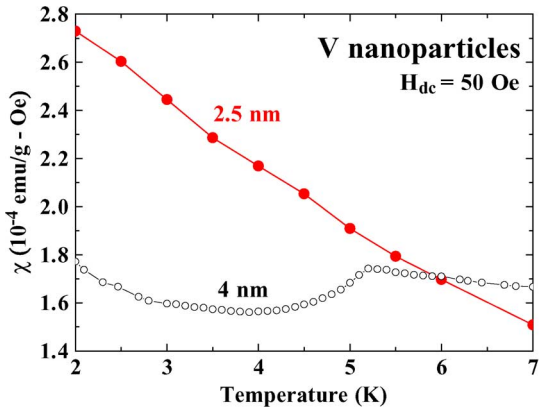

Fig. 2. Magnetic susceptibility measurements of vanadium 4-nm (hollow circle) and 2.5-nm (solid circle) nanoparticles with 50-Oe applied magnetic field. Diamagnetic signal is obtained only from the 4-nm sample.

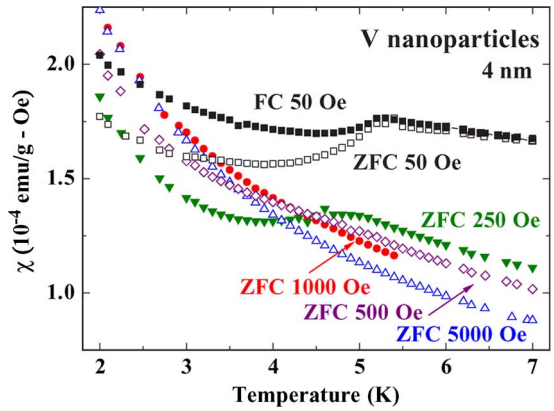

Fig. 3. ZFC process for measuring magnetic susceptibility at 50 Oe (hollow square), 250 Oe (downward solid triangle), 500 Oe (hollow diamond), 1000 Oe (solid circle), and 5000 Oe (hollow upward triangle). Result of FC test in 50-Oe (solid square) magnetic field is also shown.

4 ± 1 nm were identified. Fig. 1 shows the X-ray diffraction patterns of the 2.5 and 4 nm and bulk samples. All of the diffraction peaks can be associated with a body-centered cubic (bcc) vanadium structure. No extra impurity or oxide peak was found. As expected, the diffraction peaks were much broader than the instrumental resolution. Furthermore, Rietveld analysis reveals that both samples had a cubic structure in the 1–3-m phase. The lattice constants increased as the particle size decreased, reflecting the finite-size effect. Those of the 4- and 2.5-nm samples were 0.42% and 0.55% greater, respectively, than that of the bulk sample.

The T_C of bulk vanadium is known to be 5.38 K, and the critical magnetic field (H_C) is 1420 Oe. Fig. 2 shows the magnetic susceptibility of 2.5- and 4-nm vanadium nanoparticles in an 50-Oe applied dc magnetic field. Clearly, no superconductivity signal was observed in 2.5-nm nanoparticles above 2 K. A turning point in the magnetic susceptibility curve and a diamagnetic signal were obtained from the 4-nm sample at around 5.2 K. This curve can be regarded as the superposition of a normal state of vanadium outer shell (paramagnetism, yielding a hyperbolic curve) and a superconducting state of the inner core of the nanoparticles (diamagnetism, yielding a step function with the step at T_C). For the bulk material, the estimated 100% superconductivity signal in mass magnetic susceptibility is about -1.34×10^{-2} emu/g Oe. Here, the obtained diamagnetism signal has only about 0.13% of its estimated strength. Clearly, the finite-size effect has an important role, implying that the critical size for superconductivity is in between 2.5 and 4 nm.

Fig. 3 shows the measured magnetic susceptibility of 4-nm nanoparticles in various applied dc magnetic fields. The 50-Oe field cooling (FC) and zero field cooling (ZFC) experiments revealed the Meissner effect, and T_C was found to be approximately 5.4 K. The diamagnetic signal and T_C decreased as the applied magnetic field increased in the ZFC experiments. Clearly, the critical field of the 4-nm vanadium nanoparticles was about 500 Oe, which is only 35% that of the bulk material ($H_c = 1420$ Oe), because of the finite-size effect [10].

The single electron level spacing δ of the nanoparticles can be estimated using the Kubo theory [7], [9] since δ is inversely

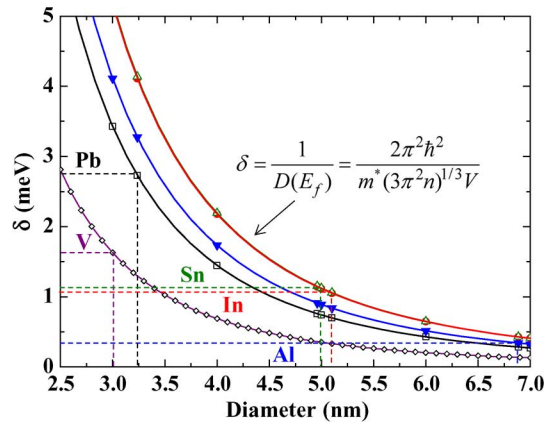

Fig. 4. The plot of single electron level spacing as a function against metal particle diameters. Critical diameters are estimated to be 3, 3.2, 5, 5.1, and 6.8 nm for V (hollow circle), Pb (hollow square), Sn (upward triangle), In (solid circle), and Al (downward triangle) metal particles.

proportional to the density of electron states D at the Fermi energy E_F

$$\delta = \frac{1}{D(E_F)} = \frac{2\pi^2\hbar^2}{m^*(3\pi^2 n)^{1/3}V} \tag{1}$$

where n denotes the electron density, m^* is the effective mass of an electron, and V is the average volume of the nanoparticles. A simple estimate can be made by assuming that the nanoparticles are all approximately spherical with diameter d.

Fig. 4 plots particle diameter as a function of δ for V, Pb, Sn, In, Al metals. Here, the Anderson criterion is applied to estimate the existence determine whether the particles are superconducting. The solid curve plots the single electron level spacing δ as the diameter declines; the dashed curve plots the BCS superconductivity gap against the corresponding diameter for each metal. For vanadium particles with diameters 4 and 2.5 nm, the calculated electron level spacing δ is 0.69 and 2.81 meV, respectively. The superconducting gap of vanadium is around 1.6 meV, which is between the δ values of the 4- and 2.5-nm

particles. This fact explains the disappearance of superconductivity in the 2.5-nm particles, and verifies the Anderson criterion. Similar behavior of other metals has been reported upon elsewhere [11], [12].

IV. Conclusion

This study finds that the critical diameter for vanadium nanoparticles is between 2.5 and 4 nm. The finite-size effect reduced H_C and shifted T_C to a lower temperature. The Anderson criterion predicts a critical diameter of 3 nm, consistent with the experimental observations herein.

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