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Magnetic Properties of bcc Chromium Fine Particles

Hiroshi Nakano and Susumu Matsuo*
School of Informatics and Sciences, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601 JAPAN
Fax: 81-52-789-4800, e-mail: nakano@info.human.nagoya-u.ac.jp
*School of Informatics and Sciences, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601 JAPAN
Fax: 81-52-789-4800, e-mail: a40230a@nucc.cc.nagoya-u.ac.jp

The dependence of magnetization of *bcc*-Cr fine particles on both magnetic field and temperature was investigated experimentally at low temperatures between 2.2 and 316K at the magnetic field below 50kOe. The particle diameter ranged from 11 to 37 nm estimated by the X-ray diffraction. Smaller particles showed larger magnetization and smaller hysteresis loop of the magnetization curve. The hysteresis loop are enlarged at lower temperatures. The size distribution of the particles was estimated on the assumption that all particles were single domain particles with uniaxial magnetic anisotropy at 2K and some particles changed to show superparamagnetism at higher temperatures. The magnetization curves were analyzed by the use of the distribution on the assumption of the ferromagnetic layer localized near the surface and the antiferromagnetic region extended to the interior on each particle.
Key words: Cr, fine particle, magnetic property

1. INTRODUCTION

bcc-Cr metal is well known to have an antiferromagnetic spin-density-wave (SDW) state below Néel temperature T_N of 310K [1]. Fine *bcc*-Cr particles have shown peculiar ferromagnetic behavior different from bulk Cr below 800K, which were interpreted in terms of a magnetically ordered state localized near the surface [2,3]. The angle resolved photoelectron spectroscopy also revealed the existence of such a surface magnetic state below 800K on Cr (100) surface [4,5]. The theoretical studies [6,7] have shown the surface magnetic layer on the Cr (100) surface originating from the enhanced electronic density of states at Fermi energy. The theoretical calculation [8] showed that the surface magnetic state is stable below 800K and an antiferromagnetic state appears in the interior below bulk T_N.

The magnetic properties of fine Cr particles at low temperatures may be interesting because the interior of the particles may be antiferromagnetically ordered below bulk T_N and the ferromagnetic surface state would interact with the inner ordered state. The magnetizing process of fine Cr particles at low temperatures might, for example, be related to the magnetizing torque proportional to the surface magnetization, whereas the restoring anisotropy energy may be related to the ordered state extending to the interior of the particles.

The magnetic susceptibility of fine Cr particles at high magnetic fields may be related to the extremity effect on the bulk magnetism [9]. This has been pointed out to give rise to a twice enhanced magnetic susceptibility in the case of the insulator antiferromagnet [9], whereas similar effects in metal magnets have not been investigated either theoretically or experimentally. The magnetic susceptibility at high magnetic fields might also be enhanced by another mechanism of the high DOS at the surface or edge of the particles which arises from the band narrowing caused by the small number of the near-neighbor atoms at such places. The present paper reports the magnetic properties of the Cr particles at low temperatures and at high magnetic fields in order to give some information about the above problems.

2. EXPERIMENTAL PROCEDURE

Spectrographically standardized Cr purchased from Johnson Matthey was evaporated in Ar gas and fine Cr particles were produced in the gas to accumulate in a soot-like form on the inner wall of a glass bell jar. They were scraped off and sealed in a quartz capsule with helium gas (99.999% purity, 0.5 atm pressure) to ensure heat conduction at low temperatures without exposure to the air. The procedure is the same as that of reference [3]. The pressures of Ar gas and the average diameters are shown in Table I, where the diameters were estimated from the integral widths of the (110) X-ray diffraction line of the fine particles after all measurements with the use of the (220) line of a Si standard sample as a reference of the instrumental resolution as shown in Fig. 1.

Table I. Condition of sample preparation.

Sample No.	Ar pressure Torr	diameter nm
N2	14	37
N4	6	28
N5	1	17
N7	0.3	11

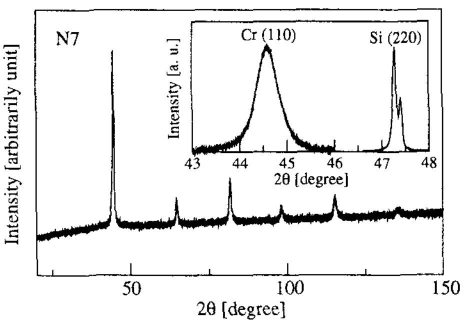

Fig. 1. X-ray diffraction pattern of N7 *bcc*-Cr fine particles. The inset shows the Cr (100) peak of N7 and the Si (200) peak of a standard sample at the same measuring condition.

As accumulated samples contained *bcc*-Cr particles and δ-Cr (A-15 type structure) particles [3], the samples were heated at 800K for 4 hours to entirely transform to *bcc*-Cr particles shown in Fig. 1.

Magnetic field and temperature dependence of the magnetization was measured by an Oxford magnetic balance using Cahn 2000 electro balance below 50kOe and below 316K.

3. EXPERIMENTAL RESULTS

Figure 2 shows the magnetization σ of the fine *bcc*-Cr particles and the bulk Cr as a function of magnetic field H at the temperature T of 4.5, 200 and 316K. The curves clearly show ferromagnetic behavior such as hysteresis at low magnetic fields and saturation trend at high magnetic fields. The magnetization is larger in smaller particles. The hysteresis of samples with larger particle size remains at higher temperatures as shown in the curves of 200K (Fig. 2).

All curves do not completely saturate even at the highest magnetic field 50kOe and at the lowest temperature 2K, especially in smaller particles (Fig. 2). The differential susceptibility of the particles less than 17 nm in diameter at high fields is about 4 times as large as that of the bulk Cr, whereas that of the particles larger than 28 nm is almost the same as that of the bulk Cr. The magnetization of the smaller particles at the highest magnetic field increases with the temperature increased.

Figure 3 shows the total susceptibility $\chi_{50\mathrm{kOe}}$ of sample N7 in the temperature range from 2.2K to 200K. It is known that bulk Cr shows an anomaly at spin-flip temperature of 123K [10], but the present sample did not show any anomaly around this temperature.

4. DISCUSSION

The critical radius r_c of a single domain iron particle showing hysteresis has been estimated to be of the order of several nm [11]. The r_c of the *bcc*-Cr fine particles was roughly estimated from $1/\tau_0 = f_0 \exp\left[-(4\pi r_c^3 K_u/3k_B T)\right]$, where K_u is a first order constant of uniaxial magnetic anisotropy, the relaxation time τ_0 is about 100s and f_0 is a frequency factor on the order of $10^9 s^{-1}$ [12,13]. K_u can be obtained from $W_h = 1.98 K_u$ [11], where W_h is a hysteresis loss as shown in Fig.4, on the assumption of a randomly oriented assembly of spherical particles with uniaxial anisotropy. r_c was therefore estimated at each temperature by the use of the hysteresis loss data.

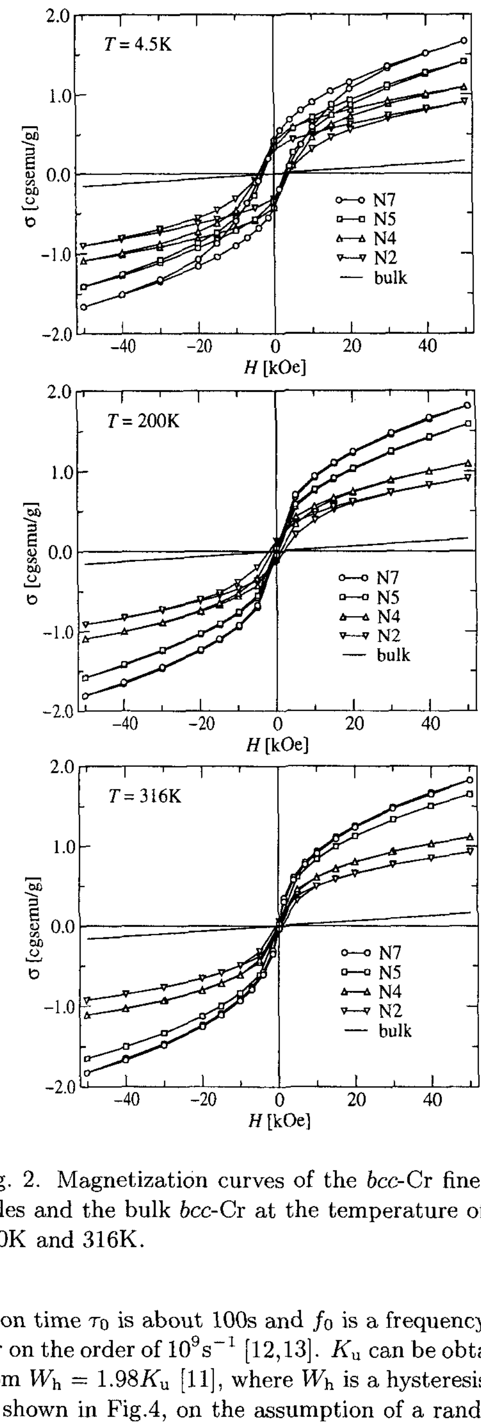

Fig. 2. Magnetization curves of the *bcc*-Cr fine particles and the bulk *bcc*-Cr at the temperature of 2K, 200K and 316K.

The saturation magnetization σ_s can be estimated from the relation $0.5\sigma_r = \sigma_s$ [11], where σ_r is a residual magnetization shown in Fig. 4. We assumed that all particles were single domain particles with uniaxial anisotropy at the lowest temperature 2.2K corresponding to r_c = 6nm and some particles changed to show superparamagnetism at higher temperatures. The magnetization curves at higher temperatures are therefore a superposition of the curves of the uniaxial anisotropy, the superparamagnetism and the an-

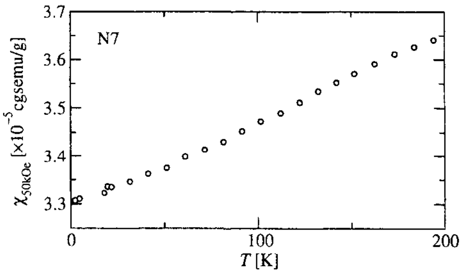

Fig. 3. Temperature dependence of the total susceptibility of sample N7.

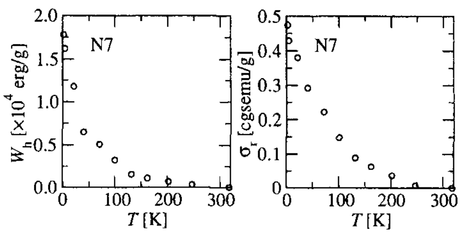

Fig. 4. Temperature dependence of the hysteresis loss W_h and the residual magnetization σ_r of sample N7.

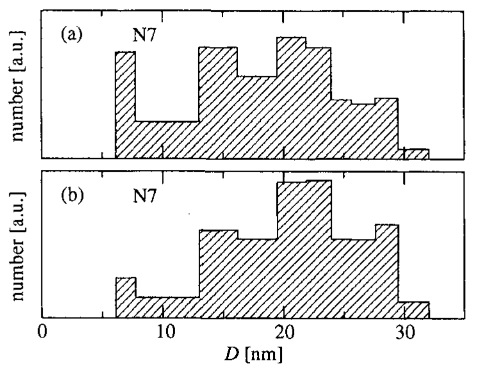

Fig. 5. Size distribution of the fine particles calculated as the magnetic moment of a particle is proportional to (a) the volume and to (b) the surface.

tiferromagnetism. The uniaxial anisotropy only gives hysteresis and the size distribution of particles can be estimated from the ratio of $\sigma_s(T)$ and $\sigma_s(2.2\text{K})$. The distribution was estimated in two cases; the magnetic moment of a particle is proportional to (a) the volume and to (b) the surface as shown in Fig. 5, where the $D = 2r$ is a diameter. The averaged diameters were 18 and 20 nm respectively and the value estimated from X-ray diffraction were 11 nm as shown in Table I. These values are in the same order but the difference is about two times. The distribution estimated in the case of (b) was used for further analyses, because the ferromagnetic layer was predicted to be localized near the surface by theories [6–8] and other experiments [2–5] and the shape of the magnetic field dependence of $\Delta\sigma$ did not agree with the experimental curve in the case of (a), where $\Delta\sigma$ is a difference of σ between decreasing and increasing magnetic fields.

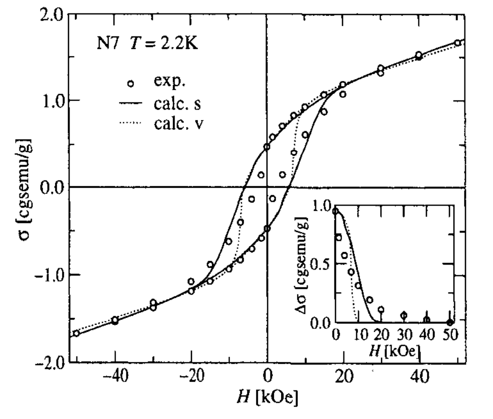

Fig. 6. Magnetization curves of N7 at 2.2K, where the solid and dotted line were calculated as the magnetization of a particle was assumed to be proportional to the surface and the volume respectively.

All particles were assumed to be single domain particles with uniaxial anisotropy at 2.2K and we estimated the magnetization curve as a superposition of the curves of the uniaxial anisotropy and the antiferromagnetism as

$$\sigma(2.2K) = \int_0^\infty \frac{f(r)\langle r\rangle\sigma_{s0}}{r} P\left(\frac{\rho\sigma_{s0}\langle r\rangle}{K_u r} H\right) dr + \chi_{af} H \tag{1}$$

where σ_{s0} is the σ_s at 2.2K, $f(r)$ is a normalized height of distribution (b) ($\int_0^\infty f(r)dr = 1$), $\langle r\rangle = 1/\int_0^\infty (f(r)/r)dr$, $P()$ is a normalized function of the magnetization curve for a randomly oriented assembly of spherical particles with uniaxial anisotropy, $\rho = 7.14\text{g/cm}^3$ is the density of Cr and χ_{af} is a magnetic susceptibility for antiferromagnetic contributions. $P()$ has the form of $\sigma/\sigma_s = P(H/H_c)$ and can be calculated numerically [11], where H_c is a coercive force. Only χ_{af} is a fitting parameter in Eq. (1) and 1.48 $\times 10^{-5}$ cgsemu/g was obtained. This value is about 4 times as large as the value of bulk *bcc*-Cr (3.2×10^{-6} cgsemu/g [14]). Figure 6 shows the results of this fitting as solid curve (calc. s) together with the calculated curve when the magnetic moment of a particle is proportional to its volume as dotted curve (calc. v) for comparison. Although the curves of $\Delta\sigma$ in inset has no fitting parameter, the solid curve gives better fit than dotted one. It indicates that the magnetization of a particle is localized at the surface.

The magnetization curve was assumed to be a superposition of the curves of the superparamagnetism, the uniaxial anisotropy and the antiferromagnetism at higher temperature than 2.2K. The magnetization is given as

$$\begin{aligned}\sigma(T) &= \int_0^{r_c} \frac{f(r)\langle r\rangle\sigma_{s0}}{r} L\left(\frac{\mu H}{k_B T}\right) dr \\ &+ \int_{r_c}^\infty \frac{f(r)\langle r\rangle\sigma_{s0}}{r} P\left(\frac{\rho\sigma_{s0}\langle r\rangle}{K_u r} H\right) dr \\ &+ \chi_{af} H \end{aligned}\tag{2}$$

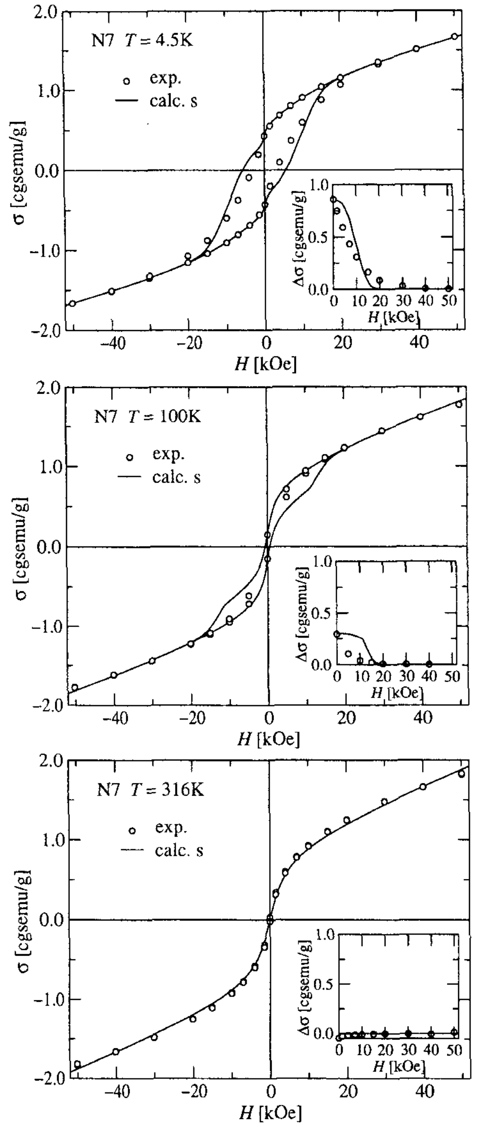

Fig. 7. Magnetization curves fitted by Eq. (2) of N7 at 4.5, 100 and 316K.

where $L()$ is the Langevin function and $\mu = (4/3)\pi r^2 \langle r \rangle \rho \sigma_{s0}$ is a magnetic moment of a particle. Only χ_{af} is a fitting parameter in Eq. (2) as same as Eq. (1). Figure 7 shows the results of the fittings of Eq. (2) for magnetization curves at the temperatures of 4.5, 100 and 316K, where the fitting parameter χ_{af} were obtained as 1.44, 1.79 and 2.00 $\times 10^{-5}$ cgsemu/g respectively in comparison with bulk's value 3.1 $\sim$ 3.3 $\times 10^{-6}$ cgsemu/g for this temperature region [14].

The curves at 4.5K and 316K have better fits than the curve at 100K. The critical diameter $2r_c = 21.9$ nm at 100K which is about the center point of the distribution (b) in Fig. 5. The roughness of the distribution can not be ignored in such a temperature region and it results in the hysteresis loop distorted. At higher temperatures, almost all the particles show superparamagnetism and it means that the first term of Eq. (2) (uniaxial anisotropy) is zero and the hysteresis disappears.

The magnetization curves of *bcc*-Cr fine particles were roughly explained with only one fitting parameter χ_{af} based on the assumption that the ferromagnetic layer localized near the surface on each particle and the total magnetization consist of the superparamagnetism (except at 2.2K), the uniaxial anisotropy and the antiferromagnetism. Antiferromagnetic susceptibility χ_{af} is much larger than bulk *bcc*-Cr and is still alive at 316K which is higher than Néel temperature 310K. This phenomena is consistent with theoretical prediction [8] the surface magnetization remaining to 3 times of the Néel temperature. Other samples have also been analyzed in the same procedure as N7 and the results were similar to N7 and the value of χ_{af} became smaller for samples with larger particle sizes.

The total susceptibility did not show any anomaly around the bulk's spin-flip temperature as shown in Fig. 3. This result is consistent with experiments of the neutron diffraction [15] which concluded that a simple antiferromagnetic structure is stabilized in the whole temperature range below the Néel temperature in contrast to the incommensurate SDW of the bulk *bcc*-Cr.

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