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LETTER TO THE EDITOR

Antiferromagnetism of Cr fine particles

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Abstract. The magnetic structure of Cr fine particles was studied by neutron diffraction. In contrast to the incommensurate spin-density wave (SDW) of the bulk Cr, a simple antiferromagnetic structure is stabilized in the whole temperature range below the Néel temperature probably due to a size effect. The results are compared with the case of the SDW in γ-Fe precipitates in Cu.

Cr is well known to have a spin-density wave (SDW) state in which the magnitude of a magnetic moment at each atomic position varies from site to site. The SDW is incommensurate with a lattice periodicity. The modulation of magnetic moments as a function of atomic positions is rather well described by a sine wave [1]. The SDW in Cr is believed to be stabilized by the nesting of Fermi surfaces and is very sensitive to disturbances such as impurities and lattice defects. On the other hand, theories predict [2–6] that the Cr atom has a large enhanced magnetic moment at the surface and the effect extends to several inner layers from the surface. Therefore, with respect to the magnetism of Cr fine particles, there are two interesting problems. One is a Fermi-surface effect which arises from the limitation of translational symmetry in the fine particles. This may affect the details of band structure in the fine particles and lead to a different magnetism from the bulk specimen. Another point of interest with the Cr fine particles is a surface magnetism. Fine particles are good systems on which to investigate surface magnetism since the surface to volume ratio is very large and the phenomena at the surface would become conspicuous. Actually, susceptibility data for Cr fine particles show a residual (uncancelled) ferromagnetic component of the surface-enhanced moment persisting up to 800 K [7].

With the above motivation, we performed neutron scattering measurements for Cr fine particles. In this letter, we report that a simple antiferromagnetic structure is stabilized in the Cr fine particles instead of the incommensurate SDW. The stability of the SDW in Cr fine particles is compared with the case of γ-Fe precipitates in Cu. A brief discussion is also given of the surface-enhanced magnetic moment.

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A Cr fine-particle specimen was prepared by evaporation in a furnace in Ar atmosphere (0.4 Torr). Evaporation particles were gathered and sealed in a quartz tube together with He gas (295 Torr at RT) without exposure to air. Since Cr fine particles as evaporated mostly have an A-15 type structure (δ phase) [8], the specimen was annealed in the quartz tube at 833 K for 5.25 h. This thermal treatment stabilizes a BCC structure. The total weight of the Cr fine-particle specimen was 0.55 g. The size of particles in the present specimen was studied by x-ray diffraction using fine particles prepared by the same procedure as the present specimen. From the Bragg peak linewidth, the mean value of the particle diameter is estimated to be 13 nm. However, judging from the example of electron microscopy data for metallic fine particles prepared by evaporation, the size distribution is considered to be rather large.

All neutron scattering measurements were carried out using the specimen as sealed in the quartz tube. Neutron diffraction measurements were performed using the 5G(PONTA) triple-axis spectrometer installed at JRR-3, JAERI, Tokai. Incident neutrons with a wavelength $\lambda = 2.442$ Å were used. Higher-order contaminations of neutrons were carefully eliminated using a thick PG filter ($\lambda/2$ component $< 10^{-5}$). The quartz tube of the specimen was sealed in an aluminium can together with He gas (760 Torr) and the temperature was lowered by a refrigerator unit. Since all measurements were performed using a PG analyser crystal, the energy resolution of the present data is 0.55 meV in FWHM.

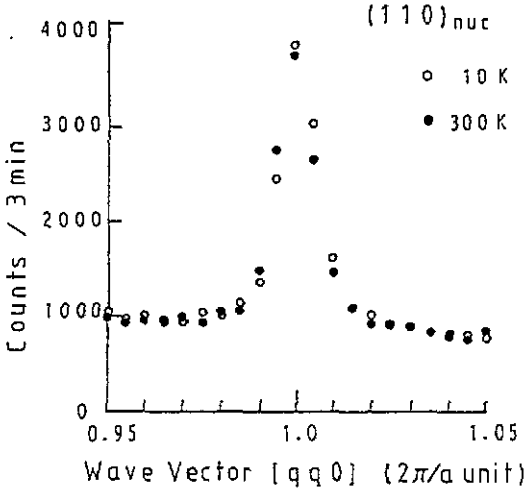

Figure 1. 110 nuclear Bragg peak of Cr fine powder observed at room temperature and 10 K.

In figure 1, diffraction patterns of the 110 nuclear Bragg peak observed at 10 and 300 K are given. The fine-particle specimen is confirmed to have a BCC structure. The temperature variation of the diffraction patterns around the 100 reciprocal lattice vector observed below 300 K is shown in figure 2. The strong background with a slope is mostly due to the quartz capsule. In this measurement, the same scans were repeated several times and the data were averaged. Since higher-order contaminations were carefully eliminated using a thick PG filter, the

observed peak at 100 is considered to be magnetic in origin. For the transverse SDW structure which is stabilized in the temperature range between 123 K and 311 K for the bulk specimen, satellite peaks with half the intensity of the 100 peak are expected around q = 0.95–0.97 and 1.03–1.05 (dotted lines in figure 2). However, no such peaks are observed within statistical errors for the present data.

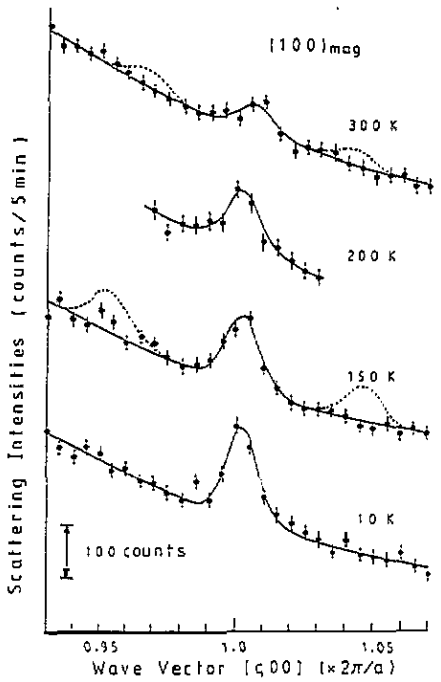

Figure 2. Magnetic diffraction patterns observed around the 100 reciprocal lattice vector at various temperatures. Solid lines indicate the fitting calculation using a square equation (background) plus single Gaussian peak. Dotted lines are the calculated satellite line profiles for the T-SDW state under the assumption that the central peak arises from the T-SDW.

Neutron scattering above 300 K was studied under different conditions from that below 300 K without using the refrigerator. Experimental data are given in figure 3. At 300 K, the 100 magnetic peak is observed clearly and the diffraction pattern is consistent with the data obtained using the refrigerator, but no well defined peaks are observed at 350 and 400 K. Since drastic changes of line profile and scattering intensity are observed in the temperature range between 300 and 350 K, the Néel temperature of the simple antiferromagnetism in Cr fine particles seems to be in this temperature range.

Bacon and Cowlam [9] studied the magnetic structure of a heavily crushed powder sample of Cr with grain size smaller than 0.1 mm. They reported that the Néel temperature of heavily crushed powder increases up to about 450 K and a simple antiferromagnetic structure (AF_0) is observed in the high-temperature range between 250 and 450 K. Below 250 K, the incommensurate SDW state is stabilized as observed in the bulk specimen. The AF_0 structure in the heavily crushed powder is

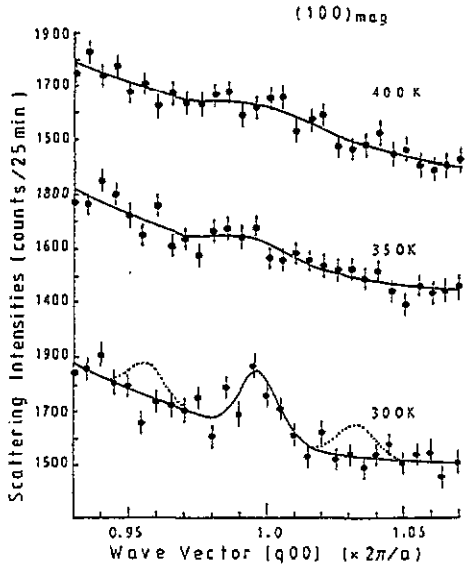

Figure 3. Observed line profiles around 100 above room temperature.

considered to be caused by the various lattice imperfections such as dislocations and vacancies since the AF_0 structure becomes less prominent and the Néel temperature goes down close to the value of the bulk specimen when the sample is annealed at high temperature. The simple antiferromagnetic structure observed in the present specimen seems not to be the case here. The present specimen is already annealed to stabilize the BCC structure and not so many imperfections are expected. The Néel temperature is far lower than that of crushed fine powder and almost the same as that of the bulk specimen. Furthermore, the incommensurate SDW state is not observed even at low temperature. This is consistent with the susceptibility data. In the bulk specimen, the anomaly of the susceptibility is observed at the spin-flip temperature $T = 123$ K, but the present specimen does not show any anomaly around this temperature.

It is interesting to compare the present results with the case of FCC (γ-) Fe and FeCo precipitates in Cu. These systems also have an incommensurate SDW state at low temperature when the crystal lattice is retained in a cubic structure [10]. One of the present authors recently studied the size dependence of the SDW state in γ-FeCo precipitates in Cu [11] and reported that the SDW for precipitates smaller than 30 nm shows the size effect. The smaller the size of the precipitates, the longer the wavelength of the SDW. However, the smallest precipitates ($d \simeq 8$ nm) still retain the incommensurate SDW state, indicating that the SDW of the γ-Fe precipitates is very stable. This is a reflection of the difference in the electronic states which stabilize the SDW in both systems. Recently, Hirai theoretically investigated [12] the mechanism of SDW formation for Cr and γ-Fe and pointed out the following differences between these systems. In the case of Cr, the antiferromagnetism is rather stable in the calculation of the magnetic phase diagram of 3d transition metals as a function of d-electron number. However, due to a special geometrical shape of the Fermi surface, the nesting of the Fermi surface lowers the electronic

energy resulting in the stabilization of the incommensurate SDW state. Accordingly, the SDW in Cr is very sensitive to the fine structure of the Fermi surface. Thus, the introduction of a small amount of impurities leads to the simple antiferromagnetic structure such as the Cr(Mn) and Cr(Fe) alloys. On the other hand, not just the electrons around the Fermi surface but almost all of the 3d electrons contribute to the SDW formation for the γ-Fe system. Thus, the SDW in γ-Fe is rather stiff against change of environment. For the Cr fine particles, smallness of the particle (limitation of the translation symmetry) supposedly disturbs the fine structure of the Fermi surface and the incommensurate SDW would become unstable.

Although the present experimental data have poor statistics, we can roughly estimate the magnitude of the magnetic moment under the assumption that whole particles are magnetically uniform. Using the intensity ratio between the 100 magnetic and 110 nuclear Bragg peaks, the magnetic moment is estimated to be $\mu = 0.59\ (\pm 0.05)\ \mu_B$ at the lowest temperature. This value is comparable to the maximum magnetic moment of the incommensurate SDW in the bulk specimen of Cr.

We have assumed here that the magnetic moment distribution in the fine particles is uniform. However, theories predict [2–6] that Cr at the surface has very large induced magnetic moment (2.2–2.8 μ_B) due to the reduced coordination number of atoms at the surface and the effect reaches up to 5–6 layers inwards. Then, for small particles like the present specimen, a considerable volume fraction of the specimen is under the influence of the surface-enhanced magnetic moment. (About 25% of the volume has more or less enhanced magnetic moments for particles with diameter $d \simeq 20$ nm.) The present experimental data at 350 and 400 K were taken to check these theoretical predictions. If the enhanced magnetic moment persists up to 800 K as reported by the susceptibility data [7] and about 25% of the volume is under the influence of the enhanced magnetic moment, a considerable amount of surface moment still remains at 350 and 400 K and magnetic scattering due to the surface-enhanced moment is expected around the 100 reciprocal lattice point. (If we assume that 30% of the volume has a moment of 1.4 μ_B, then about half of the peak intensity observed at 10 K is expected.) Weak diffuse scattering around 100 seems to exist at 350 and 400 K. This might be the contribution from the surface-induced moment. However, the statistics of the present experimental data are too poor to comment on this point. The magnetic scattering linewidth would be broadened out probably due to the smallness of the region with the enhanced moments.

Further neutron scattering measurements are now in progress for larger-size Cr fine particles. The results will be published in the near future.

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