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LETTER TO THE EDITOR

# Neutron diffraction studies on Cr fine particles

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**Abstract.** Results of neutron diffraction experiments on Cr fine particles with an average particle size of 100 nm are presented. The data are analysed using three kinds of particle showing different magnetic structures: (a) a simple antiferromagnetic structure stabilized below the Néel temperature ($T_N$); (b) a transverse spin density wave (T-SDW) state for the whole temperature range below $T_N$; and (c) a longitudinal SDW (L-SDW) state below the spin-flip temperature ($T_{SF}$) just like in bulk Cr. Since the particle size distribution is expected to be fairly large, these differences are probably caused by a difference of particle size. The spin-flip transition from the T-SDW phase to the L-SDW phase is suppressed for the intermediate-size particles ($d \simeq 100$ nm).

As is well known, Cr has an antiferromagnetic structure, whose incommensurate spin density wave (SDW) below the Néel temperature ($T_N$ = 311.5 K) is characterized by a wave vector $Q$ determined by the nesting of the Fermi surface. The spin modulation in the SDW is a transverse sine wave (T-SDW) above the spin-flip temperature ($T_{SF}$ = 123 K), and a longitudinal one (L-SDW) below $T_{SF}$. However, the SDW is very sensitive to lattice disturbances such as impurities and lattice defects.

Bacon and Cowlam [1] systematically examined the magnetic phase diagrams of different particle sizes by using heavily crushed powder samples of Cr with grain size smaller than 0.1 mm. They reported that a simple antiferromagnetic structure ($AF_0$) is observed in the high-temperature range between 250 and 450 K, and that both the L-SDW and the T-SDW structures coexist below 250 K. However, the phase diagram returns to a similar one to bulk Cr when the specimen is annealed at high temperature. Therefore, the difference of the magnetic phase diagrams between the heavily crushed powder and the bulk specimen is ascribed to lattice imperfections such as dislocations that were introduced by crushing the specimen. Very recently, one of the present authors (YT) and colleagues studied the magnetic structure of Cr fine particles with an average size of 15 nm by neutron diffraction [2]. They reported that the simple antiferromagnetic structure is stabilized in the whole temperature range below $T_N$, in contrast to he incommensurate SDW of bulk Cr. This drastic change of magnetic structure in Cr fine particles compelled us to study the magnetic structure of larger Cr fine particles.

In the present study, the magnetic structure of Cr fine particles with an average particle size of 100 nm, which were prepared by a different method, is examined by neutron diffraction.

Cr fine particles were prepared by the hydrogen plasma–metal reaction method [3]. Cr with a purity of 99.99% is arc melted in Ar gas under 0.1 MPa pressure and then the molten metal is evaporated by reactive hydrogen plasma in a 20% $H_2$–80% Ar atmosphere under

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0.1 MPa. Prior to the neutron scattering measurements, the sample is examined by x-ray diffraction and the result indicates that as-grown Cr particles prepared by this method contain about 5% $\delta$-Cr particles. Then the sample is annealed at 773 K for several hours in a pure Ar atmosphere to transform entirely to BCC Cr. In order to determine the average particle size, a dependence of the full width at half-maximum (FWHM) versus the x-ray diffraction angle was measured. The average size thus determined is about 100 nm. However, the size distribution is considered to be very large [4]. The sample was packed in a cylindrical sample holder made of an Al single crystal, and the sample holder was sealed in an Al container with He gas. All the treatments of the sample for neutron diffraction were done without any exposure to air.

Neutron scattering experiments were carried out using the 5G triple-axis spectrometer installed at JRR-3, Jaeri, Tokai. The wavelength of the incident beam was $\lambda = 2.35$ Å. A thick pyrolitic graphic (PG) filter was used in order to minimize the higher-order contamination of the Bragg reflections. A PG analyser was also used in order to eliminate the contribution from inelastic scattering. Diffraction intensities were collected by step scanning with a sampling interval of 0.005 in the magnitude of the reciprocal lattice vector $q$ by $(2\pi/a)$ units, where $a$ is a lattice constant. The accumulation time was 20 min (40 min at 290 K) for every step. The temperature of the sample was controlled in the range from 325 K to 10 K by a refrigerator.

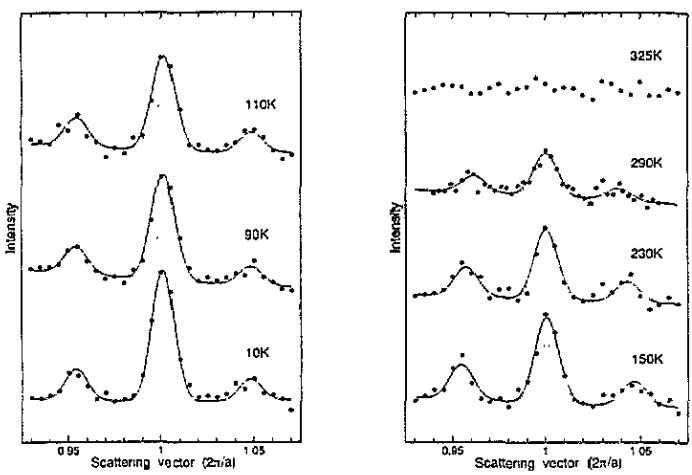


**Figure 1.** Temperature dependence of the magnetic diffraction patterns (filled circles) observed around the 1 0 0 reciprocal lattice point. Full curves indicate the fitting calculation by the least-squares method under the assumptions that there existed three Gaussian peaks and that each peak had the same FWHM. Broken curves are the calculated profiles for the contribution from the T-SDW.

Figure 1 shows the temperature dependence of the observed neutron diffraction patterns (filled circles) in the selected reciprocal lattice vectors around 1 0 0 reflections, together with the calculated results (full and broken curves). Three peaks near $q = 0.95$, 1.00 and 1.05 were clearly observed except for the profile at 325 K. Since we eliminated higher-order contaminations carefully using a thick PG filter, the observed peaks are considered to be due to magnetic scattering. On the other hand, appreciable peaks beyond statistical errors were not observed at 325 K. Thus, the Néel temperature $T_N$ of the present Cr fine particles seems to be in the temperature range between 290 K and 325 K. A remarkable difference between the profiles of a bulk specimen and the present fine particles is observed. In the bulk specimen, the satellite peaks near $q = 0.95$ and 1.05 completely disappear below $T_{SF}$, because the L-SDW structure stabilizes below $T_{SF}$. However the satellite peaks are clearly

visible even at 10 K in the present fine particles. Therefore, some particles retain the T-SDW structure even at very low temperature.

Line profile fitting calculations were performed by the least-squares method under the assumptions that there existed three Gaussian peaks and that each peak had the same FWHM. In this calculation, the intensity ratio of the left and right satellite peaks is fixed to be 1:0.7, which is estimated from an angular dependence of the magnetic form factor and the Lorentz factor. The full curves in figure 1 indicate the best fitting line profiles obtained by this calculation. The broken curves at $q = 1$ indicate the calculated line profiles for the contribution from the T-SDW state, for which a sum of the two satellite peak intensities is expected at $q = 1.0$ under the assumption of the equal orientational distribution of particles. As is clear from the figure, a residual integrated intensity exists in all temperature ranges, and the intensity suddenly increases at $T_{SF}$. Therefore, the data indicate that the simple antiferromagnetic and/or L-SDW phase coexist(s) below $T_N$ together with the T-SDW phase. However, as indicated by the previous measurement, the simple antiferromagnetic phase is stabilized in very fine particles below $T_N$. Since the size distribution of the present fine particles is fairly wide, the residual integrated intensity is ascribed to the simple antiferromagnetic phase, at least above $T_{SF}$. The temperature dependence of the integrated intensities is shown in figure 2, where open circles indicate the integrated intensity of the two satellite peaks (i.e. T-SDW) and crosses indicate the difference between the total integrated intensity at $q = 1$ and that of the satellite peaks. The notations $AF_1$ and $AF_2$ in figure 2 indicate, respectively, the T-SDW and L-SDW phases. The discontinuous change of the intensities can be found in a temperature range between 110 K and 150 K. This must be due to the fact that a portion of the present specimen shows the spin-flip transition from the T-SDW to the L-SDW phase at $T_{SF}$ as usually observed in a bulk specimen.

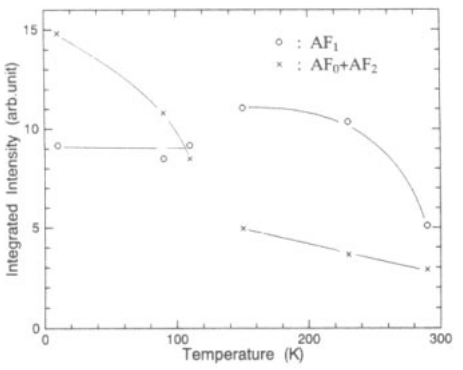


**Figure 2.** Temperature dependence of the integrated intensities of the two satellite peaks (open circles) and the difference between the total integrated intensity at $q = 1$ and that of the satellite peaks (crosses).

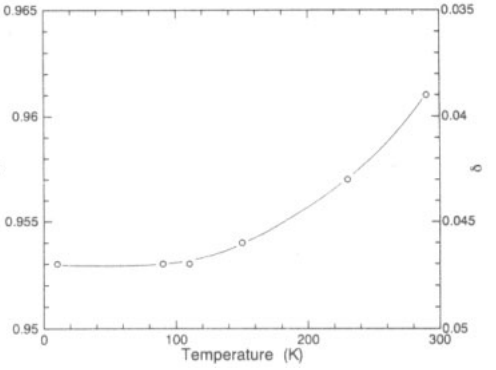


**Figure 3.** Temperature dependence of the magnitude $Q$ of the wave vector of the T-SDW. $\delta$ is equal to $1-Q$.

Thus, in the present fine Cr particles, there are three kinds of particle which show different magnetic structure:

(a) the simple antiferromagnetic structure is stabilized below $T_N$ for the smallest particles;

(b) the T-SDW phase is stabilized even below $T_{SF}$ for particles with intermediate size; and

(c) the same magnetic properties as of the bulk specimen are observed for the largest particles.

Figure 3 shows the temperature dependence of the wave vector $Q$ of the T-SDW phase. The wavelength of the SDW in the fine particles is almost the same as that in the bulk specimen.

There are several points to be noted.

(1) The T-SDW phase at the lowest temperature (4.2 K) was observed by Bacon and Cowlam [1] for both fine ($d < 0.1$ mm) and coarse ($d \simeq 0.1$–2 mm) powder Cr samples which were prepared by heavy crushing. However this phase disappeared after annealing at high temperature and the phase diagram changed to be close to that of bulk Cr, indicating that the instability of the L-SDW phase is caused by internal strain and dislocations. The present sample is already annealed to stabilize the BCC phase and is considered not to be the same as the case of Bacon and Cowlam. The Néel temperature of the present fine particles is also in the temperature range between 290 K and 325 K and rather close to the value for bulk Cr (311.5 K). Since the Néel temperature of the Cr SDW is very sensitive to lattice imperfections such as impurities and lattice strain [2], the present data indicate that the cause of the different magnetic structures in the present specimen cannot be ascribed to these lattice imperfections.

(2) Although particles with three kinds of magnetic structure are involved, more than half of the total volume shows the T-SDW state at the lowest temperature. Since the average particle size of the present specimen is about 100 nm, the particles are considered to have the T-SDW state even below $T_{SF}$. It is surprising that the spin-flip transition is suppressed for particles with a size of about 15 times the SDW wavelength. For comparison, in cubic $\gamma$-Fe precipitates in Cu, which also show the incommensurate SDW state, particles larger than 30 nm are free from the size effect [5].

(3) Furthermore, the wave vector of this T-SDW at the lowest temperature is almost the same as that of the L-SDW phase of the bulk specimen.

The wave vector of the SDW in Cr is believed to be determined by the nesting dimension of the Fermi surface, indicating that the Fermi surface of particles with intermediate size ($d \simeq 100$ nm) is almost the same as that of bulk Cr. This is consistent with the fact that the distribution of the wave vectors in the SDW is not observed although the particle size distribution is considered to be fairly broad. This point again forms a contrast to the case of $\gamma$-Fe precipitates for which the influence of the particle size on the SDW wave vector is conspicuous if the particle size is smaller than a critical size $d_c \simeq 30$ nm. In the case of Cr fine particles, the disturbance of the Fermi surface due to the smallness of the particles would be confined to very small particles in which the simple antiferromagnetic structure is stabilized. Unfortunately, we cannot estimate the critical size of the simple antiferromagnetic particles from the present data. All we know from previous work is that particles with an average size of 15 nm show the simple antiferromagnetic structure [2]. In the above discussion, we assumed uniform magnetic structure within a particle. A possibility still remains that the magnetic structure depends on the depth from the surface of the particle. However, we have no experimental data to discuss this point and leave the problem for the future.

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