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LETTER TO THE EDITOR

Searching for charge density waves in chromium

Masahiro Mori† and Yorihiko Tsunoda‡

† Department of Physics, College of General Education, Nagoya University, Chikusa, Nagoya 464-01, Japan

‡ Department of Physics, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

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Abstract. Searching for a charge density wave (CDW) in pure chromium, the satellite reflection intensity mainly due to a periodic lattice distortion (or strain wave, SW) was carefully studied at 150 K by means of x-ray diffraction. The intensity ratio of satellite peaks around the main Bragg peak does not fit the simple SW model. The discrepancy is resolved by consideration of the coexistence of the SW and CDW having an amplitude of 0.003–0.02 electrons/atom. The phase relation between the SW and CDW is also determined. The charge density distribution of the CDW seems to have greater extent in real space than that of the total electrons.

Observation of a charge density wave (CDW) does not usually involve a pure CDW but rather a periodic lattice distortion. We would like to observe the pure component of a CDW. This attempt is the first step in making the origin of the 'CDW' phase transition clear.

Chromium is well known to have a spin density wave (SDW) state below 310 K, in which the spin density varies sinusoidally in space. The period of the SDW is incommensurate and the wave vector Q is determined by the nesting of the Fermi surfaces. By means of x-ray diffraction, the present authors and colleagues [1] observed incommensurate satellite reflections whose period is one half that of an SDW instead of having the same period. Its origin is caused by the periodic longitudinal lattice modulation (strain wave, SW) like the condensation of the longitudinal acoustic phonon mode [1–3]. The property of the SW has also been reviewed by Fawcett [4]. There are two theoretical propositions as to the cause of the SW. One is the exchange striction model of Teraoka and Kanamori [5]. This point of view is that the magnetic phase transition is important. The SW is interpreted as the result of the incommensurate SDW. The other is the two-band nesting model developed by Nakajima and Kurihara [6], Kotani [7] and Hirai [8]. In their models the CDW is equal in importance to the (magnetic) phase transition and the SW is produced by the CDW.

The purpose of the present study is a search for the CDW in the limited sense, which makes an asymmetric contribution to the satellite intensities on both sides of the main Bragg peak.

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Let us consider the case that both phase modulation (= SW) and amplitude modulation (= CDW) coexist in pure Cr. As the SW in Cr is well described as a trigonometric function, the atomic position vector r_j can be written as

$$r_j = r_j^0 + \Delta \sin(2\eta \cdot r_j^0) \tag{1}$$

where $\eta = 2\pi/a - Q$, and a is a lattice constant. Δ, Q and r_j^0 are respectively a displacement amplitude which is the parallel to 2η, the wave vector of the SDW and a position vector of the jth atom in a paramagnetic state. Therefore, using equation (1), the lattice spacing ℓ_j is written as

$$\ell_j = (\ell_{j+1} - \ell_j)/2 + (\ell_j - \ell_{j-1})/2 = a + \Delta' \cos(2\eta \cdot r_j^0) \tag{2}$$

where Δ' $(= \Delta \sin(2\eta a))$ is the amplitude of the lattice spacing modulation. If CDW occurs, the atoms having the maximum lattice spacing should have maximum or minimum amplitude of charge. In short, the modulations of the CDW and the lattice spacing are in phase. Using the same phase factor given by equation (2), the total charge of the jth atom can be written by adding the CDW as

$$\rho_j(r) = \rho^0(r) + \sigma(r)\cos(2\eta \cdot r_j^0) \tag{3}$$

where $\rho^0(r)$ is the (averaged) electron density distribution function of Cr without the CDW and $\sigma(r)$ is the amplitude of the charge modulation. The phase relation between the SW and CDW has been determined uniquely as shown schematically in figure 1. In this paper, the maximum (positive) value of the CDW means that Cr atoms having the maximum lattice spacing have the excess electrons of the CDW, and the minimum (negative) spacing means that they have the deficit electrons.

Substituting equations (1) and (3) into the expression for the structure factor, we obtain the x-ray scattering amplitude F_j of the jth site as

$$\begin{aligned} F_j &= \rho_j(r)\exp(\mathrm{i}K \cdot r_j) \\ &\simeq \{\rho^0(r) + \sigma(r)\cos(2\eta \cdot r_j^0)\}\{1 + \mathrm{i}K \cdot \Delta \sin(2\eta \cdot r_j^0)\}\exp(\mathrm{i}K \cdot r_j^0) \\ &\simeq \rho^0(r)\exp(\mathrm{i}K \cdot r_j^0) + \tfrac{1}{2}\sigma(r)\{\exp(\mathrm{i}(K + 2\eta) \cdot r_j^0) + \exp(\mathrm{i}(K - 2\eta) \cdot r_j^0)\} \\ &\quad + \tfrac{1}{2}K \cdot \Delta\rho^0(r)\{\exp(\mathrm{i}(K + 2\eta) \cdot r_j^0) - \exp(\mathrm{i}(K - 2\eta) \cdot r_j^0)\} \\ &= \rho^0(r)\exp(\mathrm{i}K \cdot r_j^0) + \tfrac{1}{2}\{\rho^0(r)K \cdot \Delta + \sigma(r)\}\exp(\mathrm{i}(K + 2\eta) \cdot r_j^0) \\ &\quad + \tfrac{1}{2}\{-\rho^0(r)K \cdot \Delta + \sigma(r)\}\exp(\mathrm{i}(K - 2\eta) \cdot r_j^0). \end{aligned} \tag{4}$$

Here we have made the reasonable approximation of putting $|\sigma(r)/\rho^0(r)| \ll 1$ and $|K \cdot \Delta| \ll 1$. We have neglected the higher harmonic terms of the SW for simplicity. The x-ray scattering amplitude is obtained in the summation of equation (4) with all sites of Cr atoms. As the result of interference between both waves, we obtain the x-ray scattering intensity I as

$$\begin{aligned} I &= |\rho^0(K)|^2\delta(K - \tau) \\ &\quad + \tfrac{1}{4}|\rho^0(K)K \cdot \Delta + \sigma(K)|^2\delta(K + 2\eta - \tau) \\ &\quad + \tfrac{1}{4}|-\rho^0(K)K \cdot \Delta + \sigma(K)|^2\delta(K - 2\eta - \tau) \end{aligned} \tag{5}$$

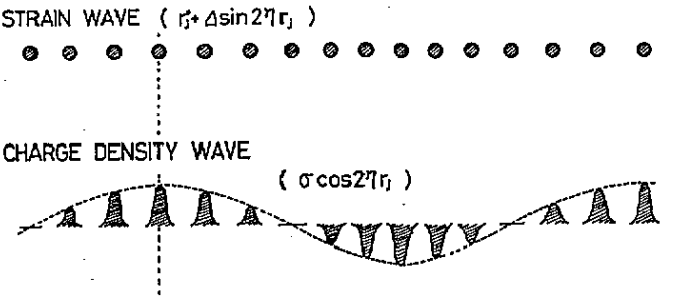

Figure 1. Schematic model of the phase relation between the strain wave (SW) and the charge density wave (CDW). The atoms having the maximum lattice spacing have the maximum amplitude of CDW in this figure.

where τ is a reciprocal lattice vector in a paramagnetic state, and

$$\rho^0(K) = \frac{1}{N}\sum_j \rho^0(r)\exp(\mathrm{i}K\cdot r_j^0)$$

$$\sigma(K) = \frac{1}{N}\sum_j \sigma(r)\exp(\mathrm{i}K\cdot r_j^0).$$

Here, the first, second and third terms in equation (5) are representative of the main Bragg reflection and the primary inside and outside satellite reflections, respectively. N is the total number of unit cells. $\rho^0(K)$ and $\sigma(K)$ are the Fourier transform of $\rho^0(r)$ and $\sigma(r)$, respectively. We have adopted the Debye temperature and $\rho^0(K)$ reported by Diana and Mazzone [9]. Thus, as a result of interference between both waves, the calculated intensity ratio of the satellite peaks around the main Bragg reflection at τ is written as

$$R'(\tau) = \frac{|\rho^0(K_+)K_+\cdot\Delta + \sigma(K_+)|^2\exp(-2B(\sin\theta_+/\lambda)^2)}{|\rho^0(K_-)K_-\cdot\Delta - \sigma(K_-)|^2\exp(-2B(\sin\theta_-/\lambda)^2)} \tag{6}$$

where K_+ and K_-, given by $\tau+2\eta$ and $\tau-2\eta$, are reciprocal lattice vectors of the primary inside and outside satellite reflections, and B and λ are the Debye–Waller factor and the x-ray wavelength. θ_+ and θ_- are the Bragg angles of K_+ and K_-, respectively.

Further correction of the Lorentz polarization factor for a partially polarized x-ray is essential. We have ignored the secondary extinction correction as the satellite intensity is too weak. The calculated intensity ratio $R(\tau)$, which we may compare with the experimental result, is written (after correction of the Lorentz polarization factor) as

$$R(\tau) = \frac{I(K_+)}{I(K_-)} = \frac{|\rho^0(K_+)K_+\cdot\Delta + \sigma(K_+)|^2\exp(-2B(\sin\theta_+/\lambda)^2)L(\theta_+,\theta_M)}{|\rho^0(K_-)K_-\cdot\Delta - \sigma(K_-)|^2\exp(-2B(\sin\theta_-/\lambda)^2)L(\theta_-,\theta_M)} \tag{7}$$

where θ_M is the Bragg angle of the monochromator. $L(\theta, \theta_M)$ is the Lorentz polarization correction factor for an x-ray with respect to the direction of the monochromator surface and the Bragg angle θ of the specimen relative to the direction normal to the flat surface. The x-ray absorption factor due to the specimen shape effect must also be added to the correction in the case of both satellites not sitting on the same θ–2θ scanning direction. Therefore, the study was restricted to measurement around the 200 and 400 reflections, being almost independent of correction. Moreover, the reappearance of the results has been confirmed by the study using several different x-ray hitting positions for several specimens.

The intensity ratio $R(\tau)$ of two peaks around the 200 reflection, for comparison with the experimental data, is calculated to be 0.942 using equation (7) after the consideration of the atomic form factor, Lorentz polarization factor and Debye–Waller factor, assuming $\sigma(K) = 0$ and $\Delta = 0.002a$ which is a value reported by previous authors [1–3]. The intensity ratios of satellite peaks around some Bragg reflections calculated in two typical cases, 'no CDW' and 'CDW(0.01)', are shown in table 1. Given there are the calculated intensity ratios in the cases of 0 and 0.01 CDW electrons/atom, respectively, behaving similarly to the total Cr electrons coexisting with the SW. The upper and lower values in the same column correspond to the cases in which Cr atoms having the maximum lattice spacing have the maximum amplitude of CDW, and vice versa.

Table 1. Calculated intensity ratios $R(\tau)$ of satellite peaks around main Bragg reflections using equation (7) and the values from [9] (left-hand columns) with Cu $K\alpha_1$ (Mo $K\alpha_1$) radiation. 'SW only' and 'CDW(0.01)' indicate the intensity ratios calculated on the assumption that the CDW amplitudes are 0 and 0.01 electrons/atom, respectively, with the same form factor as the total electrons of Cr coexisting with the SW of $\Delta = 0.002a$. The upper and lower values (SW+CDW) correspond to the cases that Cr atoms having the maximum lattice spacing have the maximum amplitude of CDW and vice versa. The right-hand columns are calculated using equation (7) and the scattering amplitudes from [10].

	Calculated with values from [9]		Calculated with the values from [10]	
	200	400	200	400
SW only	0.942 (0.961)	(0.941)	0.925 (0.943)	(0.935)
SW+CDW(0.01)	0.882 (0.899)	(0.911)	0.865 (0.882)	(0.905)
SW+CDW(−0.01)	1.007 (1.027)	(0.973)	0.988 (1.008)	(0.967)

Single crystals of Cr grown from the vapour of chromium iodide were used. The sample surface was cut with a diamond cutter to be normal to [100] within an error of 1°. As the magnetic properties of Cr are very sensitive to strain, the cut surfaces should be removed. Therefore, they were heavily etched with a dilute HNO_3–alcohol solution, keeping the surface as flat as possible. This is important for the correction of the Lorentz polarization factor and specimen shape effect. But the samples still had considerable surface roughness. The study was carried out with a conventional double-circle diffractometer, using Cu $K\alpha_1$ and Mo $K\alpha_1$ radiations monochromated with pyrolitic graphite. The x-ray generator with a fine-focus x-ray tube was used at 45 kV and 25 mA. In order to reduce thermal diffuse scattering, a fine collimation system was used. A slit of 0.2×3.0 mm^2 was set at 250 mm behind the specimen. An

aluminium filter with suitable thickness was utilized in order to eliminate the strong fluorescence in the study using Cu Kα radiation. The sample was cooled by blowing cold N_2 gas and kept at 150 ± 0.2 K. Samples with surfaces normal to [100] were used for measurements around the 200 and 400 reflections.

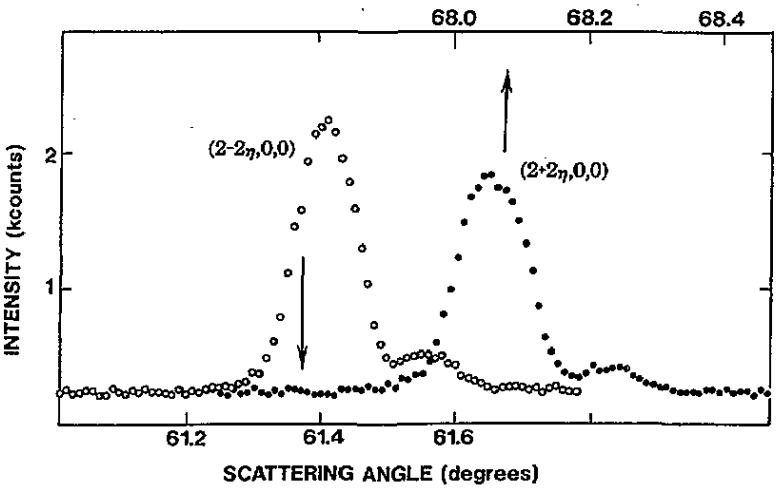

Figure 2. The intensity profiles of the primary satellite reflections around the 200 reflection observed at 150 K with a θ–2θ scan using Cu Kα_1 radiation. A small bump at the higher angles is due to the same satellite reflection by the Cu Kα_2.

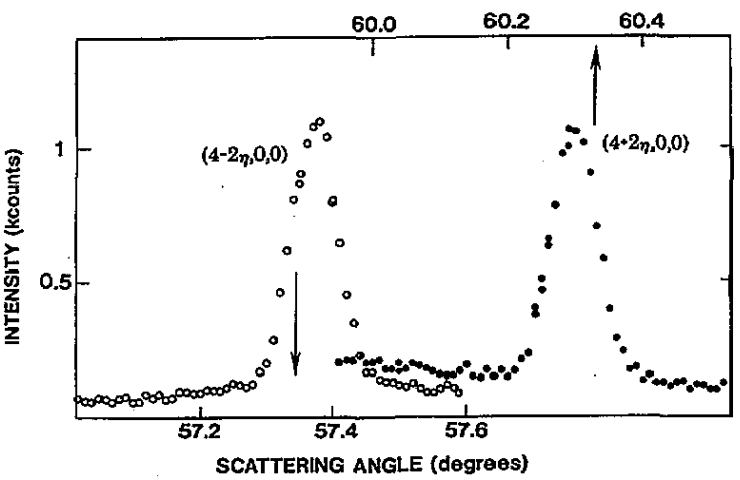

Figure 3. The intensity profiles of the primary satellite reflections around the 400 reflection observed at 150 K with a θ–2θ scan using Mo Kα_1 radiation.

Figure 2 shows the intensity profiles of both satellite reflections observed around the 200 reflection. This pattern was obtained by θ–2θ step scanning using Cu Kα_1

radiation. A small bump at the higher angles is due to the same satellite reflection by Cu $K\alpha_2$ radiation which was minimized using the fine-slit system. The observed intensity ratio $R(200)$ is 0.907 ± 0.007. Figure 3 shows the intensity profiles of both satellite reflections observed around 400. This pattern was obtained by the same scanning using Mo $K\alpha_1$. The observed intensity ratio is 0.934 ± 0.010. The observed intensity ratios of the satellites around the main reflections are summarized in table 2 as the study with several samples. All the observed intensity ratios are less than those estimated from the model with $\sigma(K) = 0$ (SW only). This strongly suggests the existence of a charge density wave modulation in Cr below the Néel temperature. The phase relation between the SW and CDW is like the case where Cr atoms having the maximum lattice spacing have the maximum amplitude of CDW.

Table 2. Observed intensity ratios $R(\tau)$ of satellite peaks around the main Bragg reflections with Cu $K\alpha_1$ (Mo $K\alpha_1$) radiation at 150 K. The error was estimated statistically.

Reflection	Observed $R(\tau)$			
200	0.912±0.010	0.907±0.009	0.907±0.007	(0.908±0.010)
400	(0.934±0.015)	(0.930±0.010)		

The parameter $\sigma(K)$ can be determined inversely from the intensity ratios summarized in tables 1 and 2. Figure 4 shows the observed $\sigma(K)$, the so-called form factor of the CDW, deduced from the experimental data and the left-hand columns of table 1. Solid and open circles are the measurement points using Cu $K\alpha_1$ and Mo $K\alpha_1$ radiations, respectively. The dotted curve is the form factor of total electrons of Cr normalized at $\sigma(0) = 0.006$ [9, 10]. The solid curve is the same for the 3d electrons normalized at $\sigma(0) = 0.013$ [10]. The observed form factor seems to be between these form factors. The phase relation between the SW and CDW does not depend on the model, but the amplitude of the CDW depends on the amplitude of the SW and the scattering amplitude of Cr as shown in table 1. Therefore, it is difficult to estimate the amplitude and the form factor of the CDW accurately.

In summary, the measurement of the satellite reflection intensity in Cr was carried out carefully at 150 K, with results as follows. In order to observe the small CDW, the asymmetric contribution to the intensity of satellite reflection depending on the side was artfully utilized. This is due to the coexistence of both phase (SW) and amplitude (CDW) modulations in a real incommensurate lattice system. The experimental result of intensity ratios strongly suggests the existence of the CDW modulation in Cr. The phase relation between the SW and CDW determined from the experimental data is that Cr atoms having the maximum lattice spacing have the maximum amplitude of CDW. It may safely be said that the maximum amplitude of the CDW is estimated to be 0.003–0.02 electrons/atom from the present data, although the value mainly depends on the x-ray scattering amplitude of Cr as shown in table 1. The charge density distribution seems to have greater extent in real space than that of the total electrons.

Measurement around the 110 reflection was also done using the sample with a [110] surface, but the values of the intensity ratio varied, being sensitive to the sample surface. We must be careful about the value of the CDW amplitude because the estimation depends sensitively on the correction factors. The most serious source

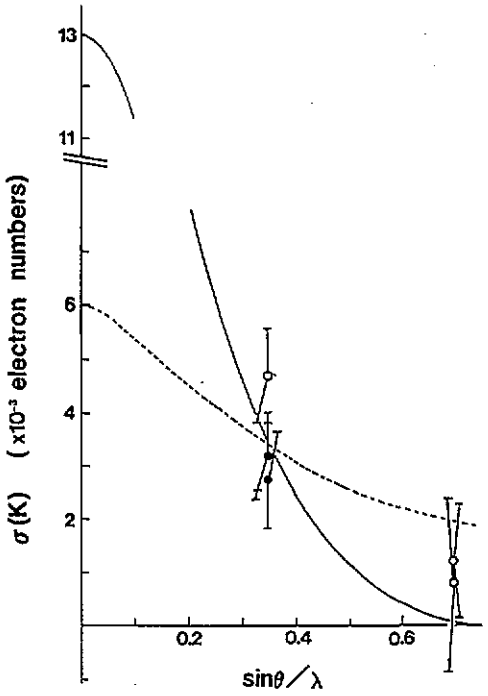

Figure 4. The K dependence of σ, the so-called form factor of the CDW. The solid and open circles are the measurement points using Cu $K\alpha_1$ and Mo $K\alpha_1$ radiation, respectively. The dotted curve is the form factor of the total electrons of Cr normalized at $\sigma(0)=0.006$. The solid curve is the form factor of the 3d electrons normalized at $\sigma(0) = 0.013$. The statistical error is shown with a bar on each circle.

of ambiguity in the most important experimental result $R(110)$ comes from the correction of the x-ray absorption factor. This sample shape correction conflicts with the need for heavy etching in order to remove the stressed surface. One method to avoid such corrections may be conducting the experiment using a stress-free sample, whose size is less than the absorption constant.

In order to determine the character of the CDW, many more x-ray studies are necessary, though they are very difficult. Moreover, the CDW is not produced only in the case of the latter theory [6–8], but may also be produced in the former [5], as the rearrangement of the charge probably exists as the result of the SW caused by SDW. This makes the discrimination of theories more difficult. Knowledge about the CDW is very important for the good understanding of the ground state of Cr.

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