# Neutron-Diffraction Investigation of Chromium with Small Additions of Manganese and Vanadium\*

## Y. HAMAGUCHI,<sup>†</sup> E. O. WOLLAN, AND W. C. KOEHLER Oak Ridge National Laboratory, Oak Ridge, Tennessee (Received 2 December 1964)

The magnetic properties of chromium alloys with small amounts of manganese (0.5%, 0.74%, 2.1%) and vanadium (1.0%, 1.9%) have been investigated by neutron diffraction, and these results and others involving higher manganese concentrations are compared with theoretical calculations by Tachiki and Nagamiya. The addition of vanadium tends first (1.0%) to destroy the long-range modulation of the moment configuration and then rapidly to eliminate the magnetic moment of the system. The addition of manganese progressively modifies the temperature-dependent properties of the modulated-moment structure of pure chromium and the temperature of the spin-flip transition. Over a small composition range both the simple antiferromagnetic and the modulated-moment structures appear to be stable. Above 2.1% manganese only the simple antiferromagnetic structure is observed. The changes in the magnetic properties of the alloys have a qualitative relation to the theoretical calculations.

#### INTRODUCTION

**C**INCE the early work of Shull and Wilkinson,<sup>1</sup> who **D** showed that metallic chromium is antiferromagnetic, it has become apparent in a number of later studies<sup>2-6</sup> that the magnetic properties of this metal are much more complicated than the early neutrondiffraction measurements on powder samples had indicated. Corliss, Hastings, and Weiss<sup>2</sup> first showed by measurements on a pure single crystal that a long-range modulation is superimposed on the otherwise simple antiferromagnetic structure and that the Néel temperature of their sample coincided closely with anomalies in other physical properties such as electrical resistivity, magnetic susceptibility, specific heat, etc. After the discovery of the modulated-moment type of antiferromagnetism<sup>7</sup> it was shown by Shirane and Takei<sup>5</sup> that the long-range modulation in chromium must be of this type over part of the temperature range. at least, and not of the antiphase-domain type originally<sup>2,3</sup> proposed. This latter conclusion follows from their determination of the absence of third-order satellites in the neutron pattern. The conclusion is also related to the existence of a spin-flip transition in chromium. Starting at the Néel temperature the spins are perpendicular to the wave vector of the modulation but at about 120°K the spins change their orientation and lie along the wave vector. At the higher temperatures a spiral-type structure is compatible with the observations.8 The spin-flip was first observed by Bykov et al.<sup>4</sup> although it was not originally interpreted as such. Another experiment was performed by Wilkinson et al.<sup>9</sup> who concluded that no local magnetic moment exists above the Néel temperature.

Several theories<sup>10-13</sup> have been proposed to explain the unusual magnetic properties of chromium. They are based on band-theoretical calculations, the most important feature of which is the relation between the Fermi surface and the Brillouin-zone boundaries of the band electrons. It is thus of interest to examine how the magnetic properties are modified by changes in the Fermi level or the Brillouin-zone boundaries. As shown by electronic specific-heat measurements<sup>14</sup> the introduction of small amounts of Mn, Fe, and V into Cr should change the Fermi level, but the Brillouin-zone boundaries will be little changed since dilute alloys of such elements with Cr retain the same bcc crystal structure with almost the same lattice spacing. The temperature at which the electrical resistivity shows an anomaly in Cr is very sensitive to the amount and kind of element added. This temperature is especially sensitive to the addition of manganese and vanadium. In Cr-Mn alloys, de Vries<sup>15</sup> has shown that 1 at.% of Mn raises the temperature of the resistance anomaly to 460°K, and Hamaguchi and Kunitomi<sup>16</sup> have shown

- <sup>14</sup> A. W. Overhauser, Phys. Rev. 128, 1437 (1962).
   <sup>12</sup> K. Yosida, Progr. Theoret. Phys. (Kyoto) 28, 759 (1962).
   <sup>13</sup> M. Tachiki and T. Nagamiya, Phys. Letters 3, 214 (1963).
   <sup>14</sup> C. H. Cheng, C. T. Wei, and P. A. Beck, Phys. Rev. 120, 426
- (1960).

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<sup>&</sup>lt;sup>1</sup> Guest scientist from Japan Atomic Energy Research Institute. <sup>1</sup> C. G. Shull and M. K. Wilkinson, Rev. Mod. Phys. 25, 100 (1953).

<sup>&</sup>lt;sup>2</sup> L. Corliss, J. Hastings and R. Weiss, Phys. Rev. Letters 3, 211 (1959).

<sup>&</sup>lt;sup>(15)</sup> G. E. Bacon, Acta Cryst. 14, 823 (1961).
<sup>4</sup> V. N. Bykov, V. S. Galovkin, N. V. Ageev, V. A. Levdik, and S. I. Vinogradov, Dokl. Akad. Nauk SSSR 128, 1153 (1959) [English transl.: Soviet Phys.—Doklady 4, 1070 (1960)].
<sup>6</sup> G. Shirane and W. J. Takei, J. Phys. Soc. Japan 17, Suppl. PHIL 32 (1962)

<sup>&</sup>lt;sup>6</sup> H. Bjerrum Møller, K. Blinowski, A. R. Mackintosh, and T. Brun, Solid State Commun. 2, 109 (1964).
<sup>7</sup> J. W. Cable, E. O. Wollan, W. C. Koehler, and M. K. Wilkinson, J. Appl. Phys. 32, 59S (1961).

<sup>&</sup>lt;sup>8</sup> In a recent investigation with polarized neutrons, P. Brown, C. Wilkinson, J. Forsyth, and R. Nathans Proceedings of the Tenth Conference on Magnetism and Magnetic Materials, November 1964 (unpublished)] have found evidence in favor of two transverse oscillations rather than the helical model.

<sup>&</sup>lt;sup>9</sup> M. K. Wilkinson, E. O. Wollan, W. C. Koehler, and J. W. Cable, Phys. Rev. 127, 2080 (1962).

<sup>&</sup>lt;sup>10</sup> W. M. Lomer, Proc. Phys. Soc. (London) 80, 489 (1962).

 <sup>&</sup>lt;sup>(1900)</sup>.
 <sup>15</sup> G. de Vries, J. Phys. Radium 20, 438 (1959).
 <sup>16</sup> Y. Hamaguchi and N. Kunitomi, J. Phys. Soc. Japan 19, 1849 (1964). N. Kunitomi, Y. Hamaguchi, M. Sakamoto, K. Doi, and S. Komura, J. Phys. Soc. Japan 25, 462 (1964).

|             |        |        | A      | Alloying ele | ments (%)     |        |           |        |      |       |
|-------------|--------|--------|--------|--------------|---------------|--------|-----------|--------|------|-------|
| Sample      | Al     | Co     | Cu     | Ni           | $\mathbf{Pb}$ | Sn     | ${ m Ti}$ | V      | Mn   | Fe    |
| A (pure Cr) | 0.05   | 0.05   | 0.005  | 0.03         | < 0.02        | < 0.02 | < 0.01    | < 0.02 | 0.02 | 0.03  |
| B(Mn alloy) | 0.05   | < 0.05 | < 0.01 | 0.02         | < 0.02        | < 0.02 | 0.01      | < 0.01 | 2.1  |       |
| C(ibid.)    | < 0.05 | < 0.05 | < 0.01 | < 0.02       | < 0.02        | < 0.02 | 0.01      | 0.2    | 0.74 | • • • |
| D(ibid.)    | 0.05   | 0.05   | 0.01   | 0.02         | < 0.02        | < 0.02 | 0.01      | 0.01   | 0.50 | • • • |
| E(V allov)  | •••    | •••    |        |              | •••           | •••    |           | 1.06   |      |       |
| F(ibid.)    |        | • • •  | •••    |              |               | • • •  | • • •     | 1.93   | 0.1  |       |

TABLE I. Results of chemical analysis.

that this temperature is raised to  $800^{\circ}$ K for a 48%Mn-Cr alloy and that this temperature corresponds to the Néel temperature  $T_N$ . Below  $T_N$  the magnetic structure of Cr-Mn alloys<sup>16,17</sup> with 7 to 50% Mn is of the simple form having no satellites near the (100) superlattice line in the neutron-powder pattern. On the other hand, in Cr-V alloys, 1% of V reduces  $T_N$  to  $220^{\circ}$ K<sup>15</sup> and in a 5% V-Cr alloy it is reduced below the temperature of liquid N<sub>2</sub>.<sup>18</sup> Also, Bacon<sup>3</sup> has shown that a chromium single crystal containing 0.5% Fe and 0.16% Ni has a Néel temperature of about 26°C. It has the same satellites as in pure Cr but does not show the spin-flip transition down to 90°K, whereas pure Cr shows this spin-flip at 120°K. The only way to determine magnetic structures of the sinusoidally modulated or other complex types is by means of neutron diffraction, and it is therefore of interest to investigate by this technique the effect of the alloying elements on the magnetic structure of chromium and to compare the results with the theory.

# EXPERIMENTAL PROCEDURES

Since it is very difficult to obtain single crystals of chromium containing known amounts of alloying elements, this investigation was made on powder samples. The constituents were melted together in an argon-arc furnace and then filed and annealed at 1000°C in a hydrogen atmosphere for about 72 h.<sup>19</sup> A control sample of pure chromium which was used as the host material of the alloys was prepared in exactly the same way. There was no trace of Cr<sub>2</sub>O<sub>3</sub> in the neutrondiffraction patterns of any of the samples, and the control sample showed satellites below the Néel temperature and the spin-flip transition at 120°K. The intensity ratio of the main peak to the satellites and the separation of the satellites also showed good agreement with other results.<sup>5,7</sup>

The powder sample ( $\sim 13$  g) was contained in an aluminum capsule of  $\frac{1}{4}$ -in. diam which was mounted in the cryostat of the spectrometer. Since it was difficult

to raise the temperature above 150°C in this apparatus, the Néel temperatures of the alloys were obtained by interpolation from the electrical-resistivity data. The amount of the alloying elements and also the impurities in the various samples were determined mainly by spectroscopic analysis,19 and the results are shown in Table I.

The magnetic moment of each alloy was obtained by normalizing the integrated intensity at liquid-N2 temperature to the value for pure Cr which was taken as  $0.40 \pm 0.02 \ \mu_B.^9$ 

## EXPERIMENTAL RESULTS

In the Cr-2.1% Mn alloy no satellites are observed at any temperature between 5 and 400°K which is close to the Néel temperature of 520°K as determined from the electrical-resistivity measurements. The integrated intensity of the normal antiferromagnetic reflection increases with decreasing temperature following closely the Brillouin function for  $S=\frac{1}{2}$ . More accurate measurements with a narrower Soller slit and long counting times show no satellites at 78 or at 396°K and the linewidth of the (100) superlattice line is identical with the (110) normal lattice reflection (Fig. 1). The alloys containing higher concentrations of Mn in Cr, for example 7% Mn, 19.2% Mn, 25.3% Mn alloys, have no satellites at room temperature.<sup>16</sup> It appears then that the magnetic structure of the Cr-Mn alloys with 2.1% up to 50% Mn content is of the simple antiferromagnetic type with no long-range moment modulation. The magnetic



FIG. 1. Diffraction patterns of Cr-2.1% Mn alloy.

<sup>&</sup>lt;sup>17</sup> J. S. Kasper and R. W. Waterstrat, Phys. Rev. 109, 1551 (1958).

<sup>&</sup>lt;sup>18</sup> M. A. Taylor, J. Less-Common Metals 4, 476 (1962). <sup>19</sup> We are indebted to D. E. LaValle and R. B. Quincy of the Analytical Chemistry Division, Oak Ridge National Laboratory, for purifying and annealing the specimens, and to members of the spectroscopic laboratory for chemical analyses of them.



FIG. 2. Diffraction patterns of Cr-0.5% Mn alloy. "From Low" ("From High") means that the sample is warmed up (cooled down) from the low (high) temperature to the measuring temperature.

moments and Néel temperatures increase, in this composition range, with increasing Mn concentration.

The magnetic structure of Cr-0.5% Mn alloy is quite unusual. At or above room temperature it shows the same simple structure as the 2.1% Mn alloy and the associated magnetic moment is  $0.50\pm0.04 \ \mu_B$ . The peak height and the integrated intensity of the (100) superlattice line were observed to increase with decreasing temperature down to about 250°K. At temperatures lower than 250°K, however, the peak height of the (100) reflection begins to decrease and satellites begin



FIG. 3. Difference patterns between room temperature and 120°K of Cr-0.5% Mn alloy.

to appear. The intensities of the satellites reach a maximum at about 140°K which corresponds to the temperature of minimum intensity of the main (100) peak. The ratio of the main peak intensity to the satellite intensity at this temperature is 2:1, which is the same as that in the pure Cr powder sample. The diffraction patterns of this alloy near the (100) superlattice position are shown in Fig. 2. The separation angle of the satellites at 142°K is about 2°12′ which corresponds in a sinusoidally modulated structure to a periodicity of 28.6 unit cells (Fig. 3). This periodicity is longer than that of pure Cr at 120°K which is about 20 unit cells. Unfortunately the temperature dependence of the



FIG. 4. Temperature dependence of intensities of Cr-0.5% Mn alloy. Curves A, B, and C are the extrapolation curves from the room-temperature value based on a Brillouin function.

periodicity in this alloy could not be measured with the powder sample. Below 250°K not only the peak intensity of the main peak but also the total integrated intensity of this peak and its two satellites begins to decrease and has a minimum at about  $140^{\circ}$ K, as shown also in Fig. 4. At  $100^{\circ}$ K one observes the same diffraction pattern as at  $142^{\circ}$ K except for a slight increase of the intensity of the main peak. At 78°K the intensity of the satellites decreases and that of the main peak increases, and at about 50°K the satellites disappear. At liquid-helium temperature there is only one peak but the peak height and the integrated intensity are smaller than those at room temperature as shown in Fig. 4. The extrapolated Néel temperature of this alloy is 375°K. The curves A and B in Fig. 4 are the extrapolation curves from the room-temperature value obtained from the Brillouin function with  $S=\frac{1}{2}$ . The extrapolated values at liquid-helium temperature are about twice the measured values. The magnetic moment obtained from the integrated intensity at liquid-helium temperature is 0.47  $\mu_B$ . If we had assumed that the lowest magnetic phase is a sinusoidally modulated spin wave having the spin direction parallel to the propagation vector, which is the same as that of pure Cr at low temperatures, the maximum amplitude of the spin wave is 0.67  $\mu_B$  which is in good agreement with the value of 0.68  $\mu_B$  obtained by extrapolation from the room-temperature measurement.

The reflections also show a temperature hysteresis as seen in Fig. 4. This suggests the coexistence of a hightemperature pure antiferromagnetic phase and a lowtemperature sinusoidally modulated phase and also a first-order transition between the two phases. From these observations it has been concluded that in Cr-0.5% Mn alloy there are three magnetic phases, a high-temperature pure-antiferromagnetic phase, and the two sinusoidally modulated phases, differing in spin orientation as in pure Cr. The critical temperature between the lower two phases is less well defined than in pure Cr. In pure Cr the satellites disappear over a temperature range of about 10° at 120°K in the powder sample, but in the Cr-0.5% alloy they disappear gradually over the range 100 to 45°K. In this temperature range the peak profile suggests the continuous rotation of spin direction from one perpendicular to one parallel



FIG. 5. Diffraction patterns of Cr-0.74% Mn alloy.



Fig. 6. Difference pattern between room temperature and  $128^\circ K$  of Cr-0.74% Mn alloy.

to the propagation vector when the sample is cooling down, and the integrated intensity decreases more rapidly with increasing temperature than that expected from the Brillouin function. The triangle marks of integrated intensity and peak intensity in Fig. 4 are the measured intensities at 77°K after cooling down to  $4.2^{\circ}$ K. They are higher than the values obtained when cooling down from high temperatures. This may mean the incomplete formation of coherent domains in the cooling-down process even though this was carried out over a period of more than 12 h.

In Cr-0.74% Mn alloy there are no satellites of the (100) reflection in the room-temperature pattern and the associated magnetic moment is  $0.45 \pm 0.04 \ \mu_B$ . The peak profiles at several temperatures are shown in Fig. 5. The temperature dependence of the integrated intensity, and the intensities at the maxima of the main peak and a satellite peak are shown in Fig. 6. The following differences are observed in the magnetic behavior of the 0.74% Mn alloy and of the 0.5% Mn alloy. In the 0.74% Mn alloy the satellites persist down to 5°K which means that the spin-flip transition is not complete. The intensities of the satellites are less than half of the main peak intensity even at its minimum value, and the integrated intensity at 4.2°K is more than half of the intensity determined by extrapolation from the room-temperature value. If we assumed from the data at 128°K that about a quarter of the integrated intensity comes from the pure-antiferromagnetic structure and another three-quarters comes from the sinusoidal structure having a spin direction perpendicular to the propagation vector, one obtains 0.66 for the ratio of the measured integrated intensity at 5°K to the extrapolated value, and this is quite comparable to the measured value of 0.55 for the 0.5% Mn alloy. This evidence suggests the coexistence at the low temperature of two phases, a pure antiferromagnetic phase and a sinusoidally modulated phase. In support of this is the fact that the area of the hysteresis loop is larger than that in the 0.5% Mn alloy, and in the cooling down



Fig. 7. Temperature dependence of intensities of Cr-0.74% Mn alloy. Curves A and B have the same meaning as in Fig. 4.

process the high-temperature phase persists to lower temperatures than in the 0.5% Mn alloy.

From the evidence reported here the following conclusions can be drawn regarding the magnetic-structure transitions in the Cr-Mn alloys. The magnetic structure of Cr near room temperature is made less stable by the addition of small amounts of Mn and the simple antiferromagnetic structure phase begins to appear. The stability of the simple antiferromagnetic phase increases with increasing Mn concentration, and there is an associated increase in the magnetic moment and of the Néel temperature which reaches about 800°K for



FIG. 8. Diffraction patterns of Cr-1.0% V alloy.

the 50% Mn alloy. The sinusoidally modulated structure is still stable at low temperatures for Mn concentrations less than 0.5%. The low-temperature phase of Cr is less stable than the high-temperature phase and disappears in the 0.74% Mn alloy. The high temperature phase disappears in the 2.1% alloy.

We have also studied some Cr-V alloys which are of interest because vanadium is to the left of Cr in contrast to Mn which is on the right in the periodic table. In the Cr-1.0% V alloy, for which the Néel temperature is estimated to be  $220^{\circ}$ K<sup>15,18</sup> from the electricalresistivity measurements, there is observed a simple phase from  $T_N$  to 4.2°K, the structure being the same as for the high-temperature phase of pure Cr. The diffraction pattern at 77°K and its difference pattern from room temperature, are shown in Figs. 8 and 9. The associated magnetic moment in this case is very small,  $0.28\pm0.03 \mu_B$ , and the separation of the satellites is about 3°16', which corresponds to a periodicity of 13.2 unit cells. In the 1.9% V alloy, the diffracted intensity



Fig. 9. Difference pattern between room and liquid-N\_2 temperature of Cr-1% V alloy.

is too small to detect as peaks and the magnetic moment is estimated to be less than 0.1  $\mu_B$ .

#### DISCUSSION

On the basis of his theory of spin-density waves in a free-electron gas, Overhauser<sup>11</sup> has been able to account qualitatively for some of the unusual magnetic and other physical properties of pure Cr. It appears, however, that this theory does not account for the stabilization of spin-density waves of such large amplitudes as occur in Cr. Tachiki and Nagamiya<sup>13</sup> have calculated on a band-theory basis the total energy of spin-density waves as a function of the wave vector for different  $k_F$  values. Their calculation is based on the suggestion of Yosida<sup>12</sup> that the umklapp process in the periodic lattice is essential for stabilizing the helical arrangement. They have obtained the self-consistent relation

$$\frac{g^2}{U} = \frac{1}{2N} \left( \sum^{+} \frac{\pm g^2}{(g^2 + x^2)^{1/2}} + \sum^{-} \frac{\pm g^2}{(g^2 + x'^2)^{1/2}} \right), \quad (1)$$

|                       |                   |                  |                      | ~                |                        |        |
|-----------------------|-------------------|------------------|----------------------|------------------|------------------------|--------|
| Temperature           | 2.1% Mn           | 0.74% Mn         | 0.50% Mn             | Cr               | 1% V                   | 1.9% V |
| Room                  | $0.59(AF_0)^{a}$  | $0.45(AF_0)^{a}$ | $0.50(AF_0)^{a}$     |                  |                        |        |
| Liquid N <sub>2</sub> | $0.67 (AF_0)^{a}$ |                  | ,                    | $0.40(AF_2)^{b}$ | $0.28(AF_{1})^{\circ}$ | < 0.1  |
| Liquid H <sub>2</sub> | $0.67 (AF_0)^{a}$ | 0 54             | $0.47(AF_2)^{\rm b}$ |                  | $0.28(AF_{1})^{\circ}$ | < 0.1  |
| (extrapolation)       |                   | 0.54             | 0.08                 |                  |                        |        |

TABLE II. Magnetic moment  $(\mu_B)$ .

\*  $AF_0$ : pure antiferromagnetic.

b  $AF_2$ : sinusoidal, spin  $\parallel$  propagation vector. •  $AF_1$ :sinusoidal, spin  $\perp$  propagation vector.

where U is the intra-atomic Coulomb integral, which might be about 3 eV if the correlation effects were taken into account; g is the exchange potential of the electrons due to atoms on a lattice point; and  $x=\frac{1}{2}[\epsilon(\mathbf{k}+\mathbf{q}+\mathbf{K})$  $-\epsilon(\mathbf{k})]$ , where  $\epsilon(\mathbf{k})$  is the unperturbed one-electron energy. The actual calculation has been made with some assumptions and the results are shown in Fig. 10, curves 1, 2, and 3. Each curve corresponds to different values of  $k_F$ , and the q value corresponding to the maximum point of  $(\epsilon_F/n)f(q)$  means a stable wavelength of a spin-density wave when 1/V is just below the maximum of  $(1/N)\Sigma^+(1/x)$ . From this figure they have shown that curve 2 corresponds to the magnetic structure of pure Cr.

In the alloy systems of Cr-Mn and Cr-V the rigidband model appears to be the best approximation for describing the electronic state of alloys as has been shown by many experimental<sup>14,20</sup> and theoretical<sup>21</sup>

TABLE III. Wave vector of sinusoidal modulation.

| Sample         | Separation | Wave vector $q$ (units of $2\pi/a$ ) | Periodicity<br>(unit cells) |
|----------------|------------|--------------------------------------|-----------------------------|
| >2.1% Mn       | 0          | 1                                    | ∞                           |
| 0.74 & 0.5% Mn | 46'        | 0.97                                 | 28.6                        |
| pure Cr        | 1°6'       | 0.95                                 | 20.0                        |
| 1% V           | 1°38'      | 0.93                                 | 13.2                        |

results. The Cr-Mn alloys contain more electrons below the Fermi energy and the Fermi level should be closer to the Brillouin zone boundary for the (100) superlattice than in pure Cr. This might correspond to the state of curve 1 in Fig. 10. In Cr-V alloys we have the opposite situation, and it might correspond to the state of curve 3. The experimental results show a fairly good qualitative agreement with this theory. For the alloys with more than 2% Mn a purely antiferromagnetic structure with wave vector of magnitude  $2\pi/a$  is stable for all temperatures below  $T_N$ . This is the situation represented by curve 1. In the Cr-1% V alloy, the qvector of the satellites has a magnitude  $0.93 \times 2\pi/a$ , which is shorter than that of pure Cr, which is 0.95 $\times 2\pi/a$ . This is represented by curve 3. From these

0.95 0.90 5, (b),*j t*(d) 0.85 0.80 0.75 0.74% Mn % V Cr 0.5% Mn 4 4 0.10 0.85 0.90 0.95 1.00 0.05 0 aq/211 VERSUS q WHERE  $f(q) = (1/N)\Sigma^{+1/N}$ CURVES OF  $(\epsilon_F/n)f(q)$ €<sub>F</sub> = 4.519 m/m \*eV n=0.5236 1.  $\pi/ak_{\rm F} = 1.000$  $\epsilon_{\rm F} = 4.387 \ m/m^{\pm \rm eV}$ n = 0.5007 2.  $\pi/ak_F = 1.015$ €F = 4.260 m/m \*eV 3.  $\pi/ak_F = 1.030$ n = 0.47924. FOR Cr - 0.5% Mn ALLOY FOR Cr - 0.74% Mn ALLOY 5. 6. FOR Cr - 2.1% Mn ALLOY

curves it appears that the change of state due to the alloying element is more sensitive to the q values than

The experimental results show another more com-

plicated behavior in low-concentration Mn-Cr alloys.

In the 0.5% Mn alloy there is a phase change from the sinusoidally modulated structure to the purely anti-

ferromagnetic structure, and it seems to be a first-order

transition. In the 0.74% Mn alloy, there is not only a

phase transformation at higher temperatures but also

even at 5°K the purely antiferromagnetic phases

coexist with the sinusoidally modulated phase. This

the theory would indicate.



<sup>&</sup>lt;sup>20</sup> B. G. Childs, W. E. Gardner, and J. Penfold, Phil. Mag. 5, 1267 (1960).

<sup>&</sup>lt;sup>21</sup> L. F. Mattheiss, Phys. Rev. 134, A970 (1964).



FIG. 11. Magnetic phase diagram of Cr-Mn and V alloys.

behavior is qualitatively explained by assuming curves 4, 5, and 6 between curve 1 and curve 2. Curve 4 corresponds to Cr-0.5% Mn alloy. At low temperatures, a maximum point of  $q=0.96\times 2\pi/a$  is more stable than for other q values. When the temperature rises, the other state with  $q=1\times 2\pi/a$  becomes more stable.

Curve 5 corresponds to the 0.74% Mn-Cr alloy, where we have two maxima of almost the same height. Then even at 5°K two phases coexist with some population and at high temperatures only the purely antiferromagnetic phase becomes stable. Curve 6 corresponds to the 2.1% Mn-Cr alloy, where at  $q=2\pi/a$ we have a maximum value of f(q), and hence at all temperatures the purely antiferromagnetic phase is more stable than the other phase. Several calculations involving the band structure and the Fermi surface of  $Cr^{10,21}$  suggest that in the (100) direction in the reciprocal lattice electrons belong to  $\Gamma_{25}'$  which has a doubly degenerate occupation near the first Brillouin zone boundary. If we assume a two-band structure with one band suitable for the simple antiferromagnetic structure and the other suitable for the sinusoidally modulated structure, and with the temperature dependence of the stability less intense in the former band than in the latter, we obtain the curves 4, 5, and 6 by assuming the proper distribution of electrons in the two bands. To justify this assumption we must have a precise calculation based on the detailed band structure of Cr, but it is almost impossible from the information we now have.

The integrated intensities of the magnetic peaks near the (100), (111), and (210) reflections in Cr and its alloys show good agreement with the calculated values

based on the same magnetic form factor as that of  $Mn^{2+}$ . This means that the 3d electrons are associated with the long-range ordering of the magnetic moments in Cr and its alloys. It has been known that the 3d electrons in Cr near the Fermi level are fairly free electron-like. The magnetic moments in Cr alloys seem to be explained by assuming that the 3d electrons having a larger k than some  $k_0$ , smaller than  $\frac{1}{2} \times (2\pi/a)$  (100), contribute to the self-consistent polarization, and the magnitude of the polarization is proportional to the energy gap produced by the spin modulation.

The magnetic phase diagram obtained from our experimental results is shown in Fig. 11. The boundaries are determined approximately from the neutrondiffraction data except the boundary between the paraand antiferromagnetic phase which is determined from the electrical resistivity measurements. Recently Komura and Kunitomi<sup>22</sup> have made a neutron diffraction investigation of a Cr-0.45% V alloy. Their results show very good agreement with our phase diagram. That the two experiments were made with different host materials, heat treatment and instruments might be taken as a qualitative confirmation of our experimental results on the Cr-V alloys also. The stable range of  $AF_2$  (see Fig. 11) is quite limited near pure Cr and at low temperatures. It may be suggested that the  $AF_2$ phase is stabilized by a small magnetic anisotropy of Cr.6,23

## CONCLUSION

Magnetic structures of Cr and its dilute alloys with Mn and V are very sensitive to the Fermi energy of these metals. The theory of Tachiki and Nagamiya gives a good qualitative explanation of their behavior, but to explain the data in more detail it must be improved by taking into account the detailed band structure of the 3d electrons in Cr and its alloys. On the other hand to obtain more quantitative experimental results would require the use of single crystal alloys.

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<sup>&</sup>lt;sup>22</sup> S. Komura and N. Kunitomi (private communication).

<sup>&</sup>lt;sup>23</sup> R. A. Montalvo and J. A. Marcus, Phys. Letters 8, 151 (1964).