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Antiferromagnetism in Chromium Alloys. I. Neutron Diffraction*

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The magnetic properties of Cr alloys containing small amounts of the transition metals V, Mn, Nb, Mo, Tc, Ru, Rh, Ta, W, and Re have been studied by powder and, in some cases, single-crystal neutron-diffraction techniques. Mn, Tc, Ru, Rh and Re, which increase the electron-to-atom ratio, also increase the Néel temperature and magnetic moment, which reach maximum values of about 700°K and $0.75\mu_B$, compared with 311°K and $0.40\mu_B$ for pure Cr. The wave vector of the magnetic structure also increases until, at a concentration of about 1%, it changes abruptly to $2\pi/a$ and the structure becomes commensurable with the lattice. The addition of V, Nb or Ta, which reduces the electron-to-atom ratio, or of Mo or W, for which it remains constant, diminishes the Néel temperature and moment and reduces the wave vector. Ta is the most effective in modifying the properties of pure Cr, followed by Nb and V, W, and Mo in that order. In all cases studied the transition temperature from a transverse- to a longitudinal-wave magnetic structure is reduced by alloying. These observations can be explained by the two-band model of Lomer, which has been studied in detail by Fedders and Martin. The wave vector of the magnetic periodicity connects electron and hole sheets of the Fermi surface and its magnitude and rate of change with electron concentration are in semiquantitative agreement with the energy-band calculations of Loucks. The Néel temperature is proportional to the ordered moment, and varies very rapidly with electron concentration in a way which can be qualitatively explained by the form of the Fermi surface. The variation of the ordered moment with temperature follows the BCS superconducting energy-gap function, as predicted by the theory.

INTRODUCTION

SINCE the first demonstration by Shull and Wilkinson[1] that metallic Cr is antiferromagnetic, there have been a considerable number of investigations directed towards the elucidation of the antiferromagnetic state in this metal. Single-crystal neutron-diffraction experiments[2–6] have shown that the structure differs slightly from that of a classical antiferromagnet, since the moments at the cube corners in the body-centered-cubic structure are antiparallel but not quite equal to those at the cube centers. The magnitude of the moment may be described by a sinusoidal modulation of wave vector $\mathbf{q}$. The wavelength of this modulation changes somewhat with temperature but is never very different from a, the dimension of the cubic cell, so that q is nearly $2\pi/a$. Below about 120°K the modulation is polarized longitudinally, so that the wave vector is parallel to the direction of the ordered moments. Above this "spin-flip" temperature the moments are perpendicular to the wave vector and the polarization is transverse. The wave vector always lies along a cube edge. In a macroscopic crystal, wave vectors along all three cube edges are generally found, but it has been shown[7] that this is the consequence of the random orientation of a large number of domains, each of which contains only one q. Neutron-diffraction studies have shown that the domain population can be drastically altered by cooling through the Néel point under stress or in a magnetic field.[8–10] A recent investigation of very pure, strain-free Cr showed that the transition at the Néel temperature is of first order.[9]

Paramagnetic neutron-scattering studies on isotopically enriched specimens have shown that there exist no localized magnetic moments in Cr above the Néel point.[11] This implies that the antiferromagnetic transition is caused by a very unusual instability of the conduction electron gas. This instability is due to the screened Coulomb interaction between the $3d$ electrons, and we shall see that the state to which it leads has many features in common with the superconducting state, although it occurs far less commonly.

The antiferromagnetic state in Cr is clearly critically dependent on the electronic band structure, and it is

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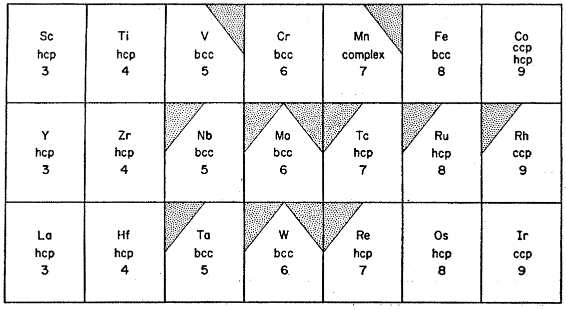

Sc hcp 3	Ti hcp 4	V bcc 5	Cr bcc 6	Mn complex 7	Fe bcc 8	Co ccp hcp 9
Y hcp 3	Zr hcp 4	Nb bcc 5	Mo bcc 6	Tc hcp 7	Ru hcp 8	Rh ccp 9
La hcp 3	Hf hcp 4	Ta bcc 5	W bcc 6	Re hcp 7	Os hcp 8	Ir ccp 9

FIG. 1. Alloy systems investigated. Shading in the upper right-hand corner indicates that single crystals were studied; in the left, powders. The number of electrons outside a closed shell, and the crystal structure for each element are indicated.

therefore of interest to study the change in the magnetic properties as the electronic structure is altered. A convenient method of accomplishing this is by the introduction of small amounts of other elements into Cr, whereby the Fermi level and electronic wave functions may be changed. A considerable literature dealing with the physical properties of such alloys, as measured on polycrystalline samples, now exists and it is well known that the magnetic ordering temperatures, deduced from anomalies in the transport properties or magnetic susceptibility, are very sensitive to the amount and kind of element added.[12] The transport properties of single-crystal specimens of dilute chromium-based alloys have recently been studied by Trego and Mackintosh, and the results appear in a separate paper[13] (referred to as II).

Until very recently, neutron diffraction experiments on the alloys had been restricted to polycrystalline specimens and to alloys of Cr with Mn and V.[14] Some work has now been reported for single crystal specimens in these systems and in the Cr-Re system.[15] Pertinent results of these studies are quoted in the appropriate sections of the text. The work reported here was undertaken as part of a systematic survey of the effects of small concentrations of various kinds of diluents on the magnetic properties of chromium. Results are presented for polycrystalline specimens of alloy systems not previously studied by neutron diffraction techniques and for a number of single-crystal specimens cut from the same ingots as those used in the transport property measurements. In some cases alloys which had been previously studied in powder form have been re-examined with single-crystal specimens.

SAMPLE PROPERTIES AND EXPERIMENTAL PROCEDURES

The types and forms of the alloy systems studied in these experiments are summarized in Fig. 1, where a portion of the periodic table is shown. A filled triangle on the left of the square denotes that powder specimens have been examined, and on the right, that single crystals were studied. In the interior of the square are given the crystal structures and the number of electrons (outside a filled shell) for each element. Except for Mn, the alloying elements have no permanent magnetic moment. For the ranges of compositions studied the body-centered cubic structure of Cr was retained by the alloys.

The polycrystalline samples used in this investigation were prepared by arc-melting the constituents in an argon atmosphere many times in order to promote homogeneity. The resulting buttons were crushed or filed and the powder was annealed at 1000°C in a hydrogen atmosphere for about 72 h, long enough to clean up any oxide contamination. As in an earlier study,[14] a sample of the high-purity iodide process chromium used as a base for the alloys was subjected to the same melting, crushing and annealing treatment as a control. As a rough analytical procedure, particularly for the alloys involving high-melting-point materials, the weight loss of the charge after melting was attributed to loss of chromium and the composition calculated accordingly. After the samples had been studied by neutron diffraction, quantitative chemical analyses were obtained.

The single crystals were grown by the arc-zone melting method described by Carlson *et al.*[16] Disks, varying in diameter from two to nine millimeters and in thickness from one to three millimeters, and oriented with a [100] direction normal to the plane of the disc were cut from the single-crystal ingot. Chemical analyses were made on portions of the ingot not used directly in the several experiments. In general the specimens were not further annealed.

The single-crystal specimens were placed in one of the ORNL low-temperature goniometers with the plane of the disc normal to the horizontal rotation axis of the instrument. Systematic scans over various regions of reciprocal space were carried out at appropriate fixed temperatures. In a number of cases, specimens of the same crystal of different diameter and thickness were studied in an attempt to establish a basis for internal calibration of the magnetic intensities. In general, however, because of the great disparity between intensities of the nuclear and magnetic reflections, and the attendant difficulty of correcting accurately for extinction, the calibrations were carried out with polycrystalline samples. Values of the product μf, where μ is the mean moment and f the form factor, were derived from low-

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[12] Complete reviews may be found in A. L. Trego, Ph.D. thesis, Iowa State University, 1965 (unpublished), and in J. G. Booth, Battelle Memorial Institute Annual Topical Report to the U. S. Office of Naval Research, 1964 (unpublished).

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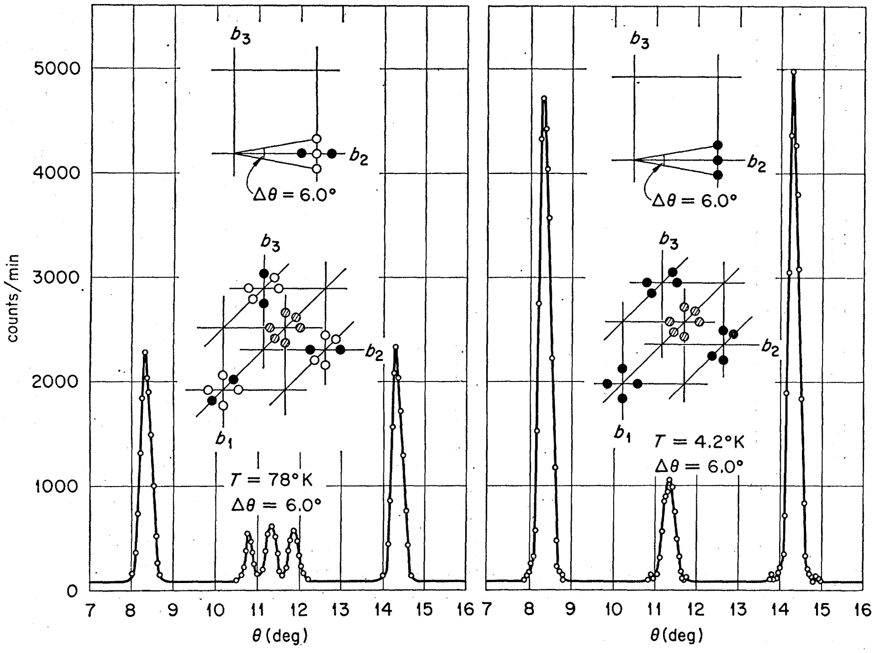

FIG. 2. Typical neutron-diffraction data for single-crystal specimens. The experimental procedure is illustrated in the sketches at the top of the figure. A schematic representation of the scattering density is shown in the diagrams in the center, and the observed data at the bottom.

temperature powder data by intercomparison of the magnetic and nuclear intensities, as well as from a calibration by a standard Ni sample. The mean moments were evaluated by means of the experimental Cr form factor.[17] Transition temperatures were measured from the temperature dependence of the intensity of an important magnetic reflection or from the temperature variation of the transport properties or both.

EXPERIMENTAL RESULTS

A typical set of single-crystal data, for a Cr-1.74% W alloy,[18] is illustrated in Fig. 2. On the left-hand side of the figure are shown the data obtained at 78°K, a schematic representation of the magnetic scattering density deduced from experiments, and a projection in the scattering plane of the scattering density around (010). The corresponding data and diagrams for a sample temperature of 4.2°K are shown in the right-hand part of the figure. The magnetic structure of this alloy at 78°K is similar to that observed for pure Cr above 120°K. The reciprocal-lattice points corresponding to the ordinary superlattice positions are surrounded by six satellites of magnetic origin.

The existence of these satellites implies a long-range modulation of the antiferromagnetic structure, the wave vector of which is parallel to one of the cube edges. The multiplicity of satellites is due to the occurrence of three domains (or wave vectors) each of which contributes one pair of satellites symmetrically disposed around the reciprocal-lattice points on reciprocal-lattice rows parallel to the wave vector. The open, cross hatched, and full circles in the diagrams represent intensities proportional to $\frac{1}{2}$, $\frac{2}{3}$, and 1, respectively, and these values result from the dependence of the scattering on the relative orientation of the scattering vector and moment direction.[19] The observations made at 78°K imply that the moments in a given domain are oriented perpendicular to the corresponding wave vector; that is to say that there is a transverse polarization of the modulation.

It is convenient to designate the positions of the satellites in terms of a deviation δ from the (0,1,0) point in reciprocal space. The satellites measured in the experimental arrangement shown in the upper diagram on the left would thus be $(0, 1, \pm\delta)$, and these are the strong peaks shown. However, with the counter opening used, there are also observed, as the crystal is rocked about b_1, contributions from $(\pm\delta, 1, 0)$ which form the central peak [second order of (020) is filtered out] and from $(0, 1\pm\delta, 0)$ which appear on either side of the central reflection. The angular separation of the $(0, 1, \pm\delta)$ satellites under the indicated conditions is 6.0°, from which can be calculated the wave vector of the modulation.

At 4.2°K, there are observed a number of changes in the rocking curves: the main satellites are approximately twice as intense as at 78°K, the intensity of the central peak is greater, and the contributions from $(0, 1\pm\delta, 0)$ are no longer observed. The scattering density deduced from experiment is shown in the insert

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[17] R. M. Moon, W. C. Koehler, and A. L. Trego, J. Appl. Phys. 37, 1036 (1966).

[18] We give compositions as atomic percent solute.

[19] For a random distribution of domain population the intensity ratios are as described above. In some of the crystals, strains developed during growth produced nonrandom domain populations, and the intensity ratios differed appreciably from those cited.

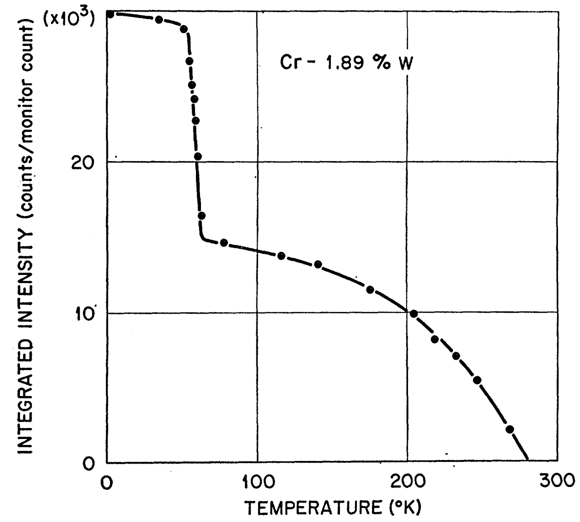

FIG. 3. Temperature dependence of intensity of magnetic satellite in Cr-1.89% W crystal. The sharp decrease near 60°K indicates the transition from longitudinal to transverse oscillation.

and the interpretation is that the polarization of the modulation has become longitudinal.

In Fig. 3 is illustrated the variation with temperature of the intensity of one of the satellites, measured as in the preceding example, in a Cr-1.89% W crystal. The spin-flip transition at 60°K is clearly indicated by the rapid rise in intensity of the satellite. A Néel temperature of about 280°K has been obtained from these data.

The results shown in Figs. 2 and 3 are more or less typical of alloys containing elements with an electron per atom ratio smaller than that of Cr, namely V, Nb, and Ta, and those with the same number of outer electrons, Mo, and W. Generally, in these alloys the Néel point is lowered, the moment value reduced, and the wave vector $q=(2\pi/a)(1-\delta)$ diminished, with respect to the corresponding quantities in pure Cr. The transverse oscillatory magnetic structure is the one usually exhibited by the alloys; the spin-flip transition is very rapidly eliminated. Observations which have been made on such alloys are summarized in the left-hand side of Fig. 4, where the Néel temperature, the spin-flip temperature, and the average magnetic moment for several systems are plotted against atomic concentration of the alloying element. For elements in the same column of the periodic table, the effect on the magnetic properties of Cr is more important the heavier the alloying element, as illustrated by the curves labeled Mo-W, and V-Ta. The diminution of the transition temperatures and magnetic moment is precipitous for alloys of those elements to the left of Cr; indeed a Cr-1.0% V alloy showed only the transverse form at temperatures as low as 4.2°K. In contrast, the changes produced by Mo and W are relatively less drastic. The spin flip transition in Cr-3.64% W is very close to 4.2°K.

In alloys with elements falling to the right of Cr in the periodic table, rather different behavior is observed and some of the results are summarized in the right-hand side of Fig. 4. The Néel temperature increases rapidly with the introduction of these elements as shown in the figure. (These data are due mostly to Booth,[12] and are obtained from resistivity and susceptibility measurements.) For alloys more concentrated than about 1.5% in any of the diluents studied, the magnetic structure of the alloy is the simple commensurable antiferromagnetic one at all temperatures above 4.2°K. For alloys with less than about 1.0% diluent, the two oscillatory structures characteristic of pure Cr are observed, but the temperature of transition between them is very much reduced. Between these two regions of concentration the commensurable struc-

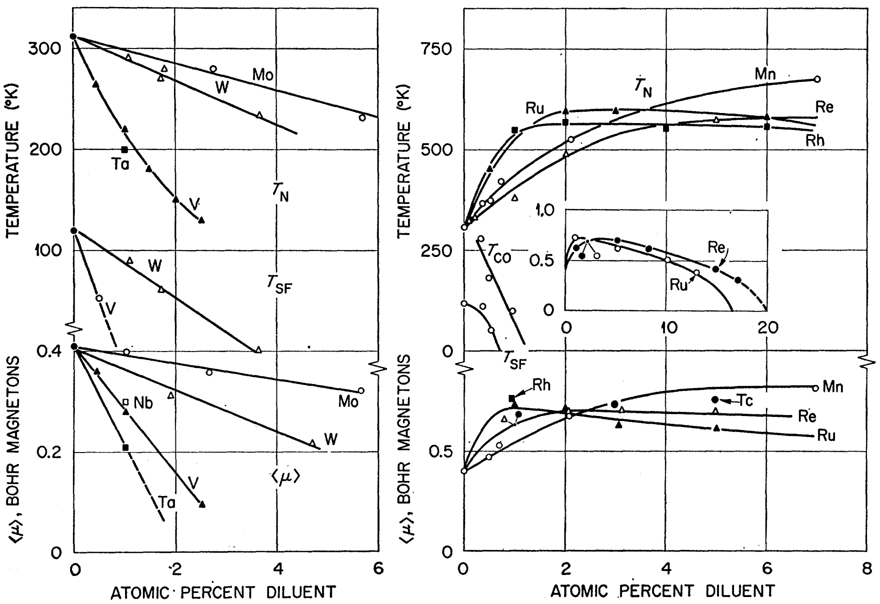

FIG. 4. Transition temperatures and average-moment values for chromium alloys. Transition temperatures are designated T_N (Néel point) T_{SF} (spin flip) T_{CO} (commensurable to oscillatory). For noncommensurable structures the symbol ⟨μ⟩ stands for the root-mean-squared moment per atom of the alloy.

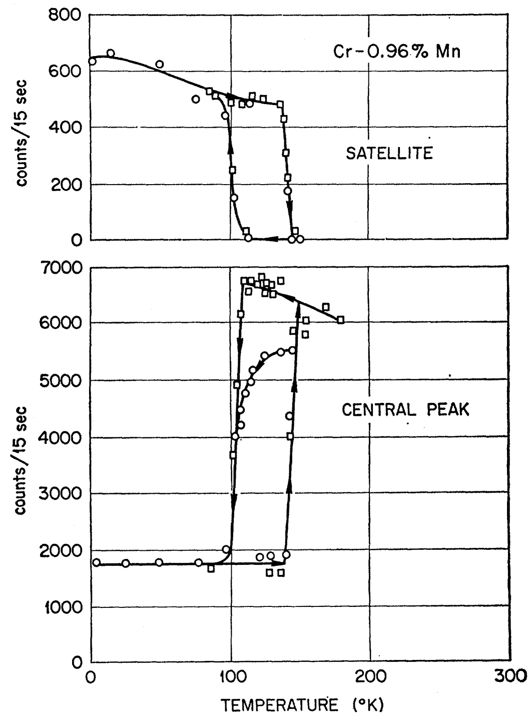

FIG. 5. The commensurable-oscillatory transition in Cr-0.96% Mn. The transition as shown is strongly history-dependent. The circles in the lower part of the figure are points taken during warm-up to a temperature at which the transformation was only partly complete and on cooling from that temperature.

ture is stable at high temperatures, the transverse oscillatory one at low temperatures. The variation with concentration of the spin-flip temperature, T_{SF}, and the commensurable-oscillatory structure transition, T_{CO}, in the Cr-Mn system is shown in the figure. Similar results have been found in the other systems as well. Thus, for example, the Cr 1.0% Tc alloy exhibited the transverse oscillatory structure at 4.2°K and the commensurable one at 77°K, and Cr-3.0% Tc the simple structure at all temperatures to 4.2°K. In Cr-0.78% Re[15] the commensurable structure observed at room temperature was found to have been replaced by the transverse one at 95°K. In one case, a Cr-0.35% Mn crystal, all three phases were observed. In this crystal the C-O transition was very close to room temperature.

The C-O transformation exhibits temperature hysteresis. The effect is illustrated in Fig. 5 where data obtained from a Cr-0.96% Mn crystal are shown. The intensity at the peak of some of the satellites and of the central reflection of a group such as that shown in Fig. 2 was measured as the temperature was raised after having first cooled the sample to 4.2°K. At 140°K the intensity of the satellites began to fall abruptly until at about 144°K it was reduced to zero. Simultaneously, the central peak grew in intensity. During the transformation the satellite spacing remained constant. On cooling from a temperature well above 140°, the reverse process set in at about 110°, and the transformation was complete at about 104°K. In one experiment, cooling was started from a somewhat lower temperature with the results shown in the lower half of the diagram.

For more concentrated alloys, the Néel temperatures in the Mn system remain constant at about 700°K for all compositions up to the equi-atomic one. In the Ru and Re alloys, however, the Néel temperatures fall rapidly toward zero at compositions near 15% and 20%, respectively. Although we are concerned in this paper primarily with dilute alloys, the results which have been obtained for concentrated alloys in the Ru and Re system are also relevant for our interpretation. In the insert to Fig. 4 are shown the magnetic-moment values derived from powder data obtained from a few of these more concentrated alloys. As shown, the moments reach a maximum after several atomic percent of Ru and Re have been introduced and then fall toward zero. In these more concentrated alloys only the simple antiferromagnetic structure has been found for the particular compositions studied.

The measurements which have been made of the wave vectors characteristic of a number of the alloy systems are summarized in Fig. 6. The quantity q varies monotonically with temperature in the alloy, as in the pure metal. In the figure this variation is exhibited by the two curves drawn for each alloy system. The upper curves refer to values measured at temperatures near the transition temperature, the lower to those obtained at temperatures very low compared to T_N. Results for the Cr-Mo system, for which rather more concentrated specimens were studied, are presented in the insert. The data given for the Cr-Re alloys has been taken from the work of Møller *et al.*[15]

For those elements which lie below or to the left of chromium in the periodic table the wave vector de-

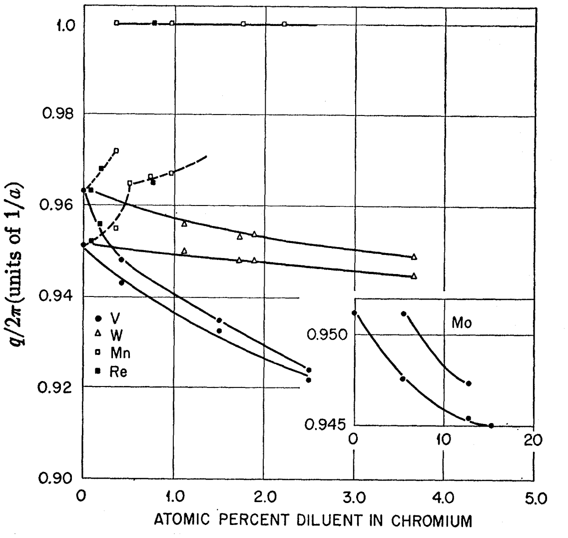

FIG. 6. The dependence of wave vector on composition for chromium alloys. A value of $q=2\pi/a$ corresponds to the commensurable structure. The upper of the two curves refers to measurements made near the Néel point, the lower to very low temperature data.

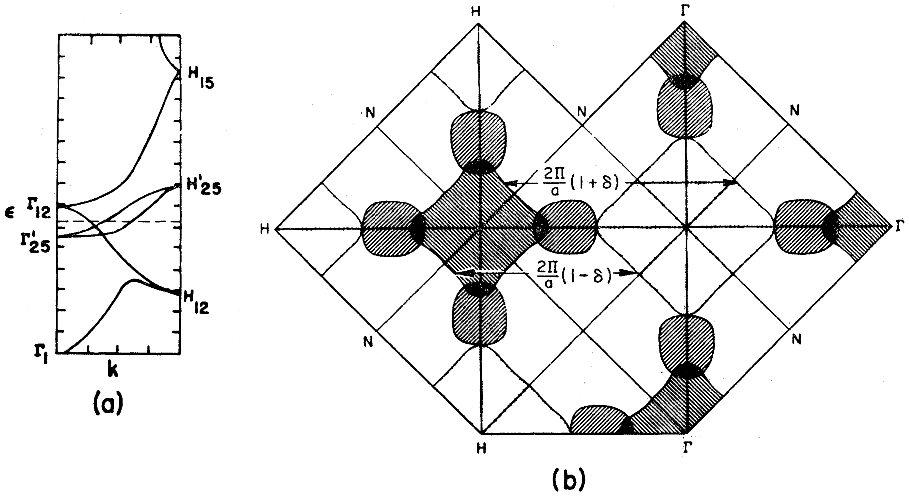

FIG. 7. The energy bands for Cr in the [100] direction and the cross section of the Fermi surface in the (100) plane (after Ref. 27).

creases with concentration, relatively slowly for Mo, somewhat more rapidly with W and very rapidly in the case of V. As Mn or Re is added to Cr, q increases slowly then changes abruptly to $2\pi/a$.

DISCUSSION

The results of our neutron-diffraction experiments have given information on the variation with concentration of the ordered magnetic moment, the Néel temperature and the wave vector of the magnetization waves in Cr alloy systems. In addition we have observed the effect on the spin-flip transition of various solutes. In this section we will attempt to interpret these results in terms of the various theories which have been proposed to account for the antiferromagnetism of Cr.

The first suggestion that the ordered moments in Cr are formed in the conduction electron gas was made by Lidiard,[20] who calculated a number of properties of such a collective-electron antiferromagnet. Overhauser[21] showed that the paramagnetic Hartree-Fock state of a free-electron gas is unstable to the formation of a spin-density wave whose wave vector is twice the Fermi radius, provided that the electrons are assumed to interact via an unscreened Coulomb force. Nagamiya *et al.*[22] studied the properties of a narrow band in which there exists a strong intra-atomic Coulomb interactioy between two electrons located on the same ion. Then concluded that a spin-density-wave state is stable under some circumstances, and that the stability of such a state is critically dependent on the electronic structure. A rather similar model was studied in some detail by Penn.[23] He considered a tight-binding band of s-like symmetry, and constructed a phase diagram of stable magnetic states. He found that spin-density-wave states were stable for some electron concentrations, and for relatively high values of the ratio of the screened intra-atomic Coulomb interaction energy to the bandwidth. Somewhat earlier Lomer[24] had discussed the band structure of Cr and suggested that the antiferromagnetic state is stabilized by the exchange coupling between two pieces of Fermi surface in different bands. As we shall see, our experiments provide strong evidence in favor of this interpretation. Fedders and Martin[25] proved that the spin-density wave state is not the Hartree-Fock ground state of an electron gas if the screening of the Coulomb interaction is taken into account.[26] They further showed that antiferromagnetism is relatively unlikely in any one-band model, and their work provides strong theoretical support for Lomer's hypothesis. They calculated a number of properties of a two-band model which approximates the electronic structure of Cr, and we shall use their results extensively in our discussion.

The reason why Cr is magnetically ordered while Mo and W, which have very similar Fermi surfaces[26] are not, is clear from, for instance, the work of Penn,[23] in which it is shown explicitly that the probability of magnetic ordering increases as the bandwidth decreases and the intra-atomic Coulomb interaction increases. The formation of a magnetically ordered state decreases this interaction energy by taking advantage of the exchange correlation of parallel-spin electrons, but results in an increased kinetic energy, due to repopulation of the **k** states. This increase is minimized however if the band width is small and the density of states correspondingly high. The energy bands for Cr in the [100] direction are shown in Fig. 7(a). The d bands in Mo and W have approximately the same form but are much broader. If spin-orbit coupling is neglected, the

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[20] A. B. Lidiard, Proc. Phys. Soc. (London) **A66**, 1188 (1953).
[21] A. W. Overhauser, Phys. Rev. **128**, 1437 (1962).
[22] T. Nagamiya, K. Motizuki, and K. Yamasaki, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965).
[23] D. Penn, Phys. Rev. **142**, 350 (1966).
[24] W. M. Lomer, Proc. Phys. Soc. (London) **80**, 489 (1962).
[25] P. A. Fedders and P. C. Martin, Phys. Rev. **143**, 245 (1966).
[26] See also D. R. Hamann and A. W. Overhauser, Phys. Rev. **143**, 183 (1966).

energy difference ($\Gamma_{12}-\Gamma_{25}'$) is calculated to be 0.134, 0.195, and 0.215 Ry in Cr, Mo, and W, respectively.[27] This increase in bandwidth with increasing atomic number, with the concomitant delocalization of the *d* wave functions and the decrease in intra-atomic interaction, explains the decreasing tendency towards magnetic ordering, manifested by the reduction in the Néel temperature of Cr containing Mo or W. The fact that the triply degenerate Γ_{25}' level lies just below the Fermi level, while the doubly degenerate Γ_{12} level is above it[28] is in accord with the form factor measurements[17] of the angular distribution of the ordered moment, which is found to have predominantly Γ_{25}' symmetry.

As has been emphasized by Lomer,[24] the precise form of the magnetic ordering is determined by the details of the Fermi surface, whose calculated cross section in the (100) plane is shown in Fig. 7(b). The flat octahedral faces of the electron jack are connected to the faces of the hole octahedron by the vectors $(2\pi/a)(1\pm\delta)$, as shown. The smallest wave vector q that describes the fundamental magnetic periodicity of the system is $(2\pi/a)(1-\delta)$ and may readily be derived from the Fermi-surface dimensions. The calculated value of q for pure Cr is $0.90\times 2\pi/a$, while the experimental value close to T_N, where the Fermi surface has not yet been significantly distorted by the magnetic order, is $0.96\times 2\pi/a$. This discrepancy is probably within the accuracy of the calculation, since the position of the faces of the electron jack is very sensitive to the choice of potential.[27]

The addition of Mn to Cr increases the electron concentration and hence causes the electron surface to expand and the hole surface to contract. This should cause q to increase, while the addition of V, on the other hand, should cause it to decrease. These qualitative predictions are in accord with the experimental results. The change in q with the electron concentration can be calculated quantitatively from the work of Loucks,[27] since he calculated the shapes and volumes of energy surfaces near the Fermi surface. Application of the rigid-band model to his results suggests that q should change by approximately 1% for each 1% of V or Mn added. The experimental results show roughly twice this rate of change of q. Again this discrepancy is probably within the calculational error, particularly as q is not calculated quite correctly for pure Cr. Indeed if one takes as the Fermi surface for Cr the set of energy surfaces which give the correct q, its rate of change with alloying is almost correctly predicted. Since the volume compensation of electrons and holes is then lost however, this calculation is not particularly meaningful. It would clearly be of interest to carry out a calculation in which the energy levels were adjusted to obtain the correct q, either by modifying the potential or by using an interpolation scheme, and then to observe its change with electron concentration. This would provide a check of the rigid-band model to quite-high concentrations, which is difficult to accomplish with other experimental techniques. A slight breakdown in the rigid-band model may be observed in the small change of q, relative to a reciprocal lattice dimension, when Mo and W are added to Cr. According to this model the location of the Fermi surface relative to the Brillouin-zone boundaries should be unaffected, but it seems that W and to a lesser extent Mo do alter the relative separations of the electron and hole surfaces by a small amount (approximately 1.5% for 10% Mo).

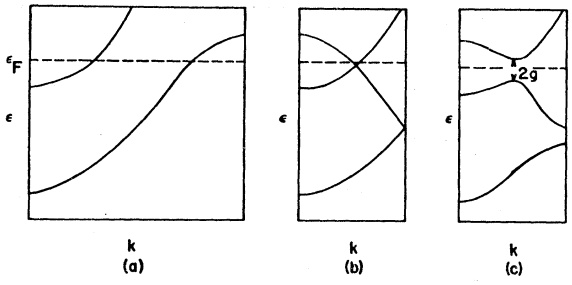

FIG. 8. Schematic representation of energy bands in an antiferromagnetic metal. (a) Paramagnetic phase. (b) Remapping due to a doubling of the period of the potential. (c) The effect of the magnetic interaction.

The onset of magnetic ordering can drastically modify the band structure and Fermi surface. As an illustration of the effects that can occur, we consider the simple example shown in Fig. 8. In the nonmagnetic phase, the bands have the form shown in Fig. 8(a) and the Fermi surface consists of electron and hole sheets of approximately the same extent. For simplicity we assume that the magnetic structure is commensurable with the lattice, so that in the ordered state the Brillouin-zone dimension in the direction of **q** is halved. The bands may be remapped into the magnetic zone, as in 8(b), and the self-consistent interaction with the ordered moment causes them to split, as in 8(c). The result is the formarion of energy gaps at the magnetic superzone boundaries, and a mutual annihilation of the electron and hole regions. If the electron and hole Fermi surfaces have almost the same shape in the paramagnetic phase, the onset of magnetic ordering turns the metal into an insulator. This is a somewhat extreme example, but we we shall show in II that a substantial proportion of the Fermi surface is annihilated by the magnetic ordering in Cr. The onset of magnetic ordering causes a sharp drop in the density of states within an energy g of the Fermi level and this behavior, which is reminiscent of that of a superconductor, is strikingly reflected in the transport properties.

The self-consistent interaction between the conduction electrons and the ordered moment causes a lowering of energy by two mechanisms. The splitting apart of

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[27] T. L. Loucks, Phys. Rev. 139, A1181 (1965) and private communication. We are very grateful to Dr. Loucks for making available to us the unpublished results of his calculations.

[28] L. F. Mattheiss, Phys. Rev. 134, A970 (1964).

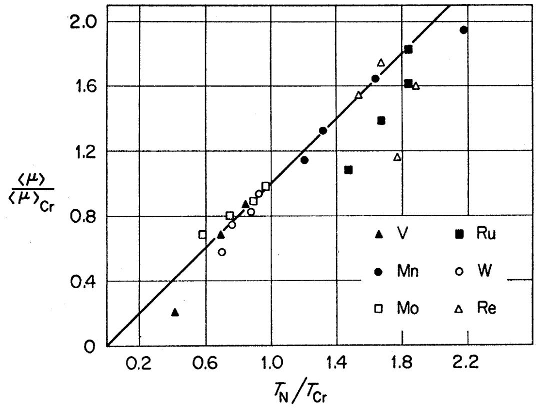

FIG. 9. The relative moment as a function of the relative Néel temperature for a number of Cr alloys. Those points for Mn, Ru, and Re which lie significantly below the line correspond to commensurable magnetic structures.

bands which cross near the Fermi level depresses the energy of filled states while raising that of empty states, and this favors a **q** which connects two pieces of Fermi surface, leading in general to an incommensurable structure. In addition the formation of a spin-ordered state reduces the intra-atomic Coulomb repulsion and thus depresses the energy of the whole of the d bands. This effect is maximized by having a large moment at all the ionic positions, where the d wave functions have large amplitude, and this can only be accomplished in a commensurable structure. In Cr the electron and hole surfaces do not run precisely parallel, so that there will be a range of q values which connect them, and the equilibrium q will be that which connects the largest area. As Mn is added, q approaches $2\pi/a$ and at some concentration the energy reduction for the incommensurable structure will become less than that for a commensurable structure, since the latter will minimize the Coulomb interaction while still connecting substantial areas of the electron and hole surfaces. At this concentration the structure will change abruptly to the commensurable simple antiferromagnetic phase. The effect of the band splitting is temperature-dependent, since the energy will be reduced in any region where the remapped bands [see Fig. 8(b)] cross within about g of the Fermi level, and g is proportional to the ordered moment.^{25} It is possible therefore that the incommensurable structure may be found at low temperatures, where a large area of Fermi surface is annihilated, while at high temperatures, where only a small area is affected, the commensurable structure is stable. This behavior is observed at intermediate concentrations in Mn and Re alloys.

We now consider the dependence of the Néel temperature and ordered moment on electron concentration and the nature of the solute. Fedders and Martin^{25} analyzed in detail an isotropic model in which two spherical pieces of Fermi surface with radius k_c in different bands are connected by a wave vector q. They show that the Néel temperature for such a system is given by an equation of the form

$$T_N = T_0 \exp(-1/\lambda), \tag{1}$$

where T_0 is a function which depends on the band structure and

$$\lambda = \gamma^2 V(0) k_c^2 / 2\pi^2 v. \tag{2}$$

Here γ is a mean overlap matrix element for electrons in the same band, $V(0)$ is the average screened Coulomb potential, given by $4\pi e^2/q_{FT}^2$ in the Fermi-Thomas approximation and v is the arithmetic mean of the Fermi velocities in the two bands. The energy gap at the Fermi surface, which is linearly related to the moment, is given by

$$g(T=0) = 1.76(v/\bar{v})kT_N, \tag{3}$$

where $\bar{v}$ is the geometric mean of the velocities in the two bands. The magnitude of the gap can be deduced approximately from the transport properties, and will be discussed in II. In Fig. 9 we have plotted the relative moment against the relative Néel temperature for those alloys for which we had sufficient information. Most of the points lie on the line

$$\langle\mu\rangle/\langle\mu\rangle_{Cr} = T_N/T_{Cr} \tag{4}$$

as expected from Eq. (3). Those points for Mn, Ru, and Re which lie below the the line correspond to commensurable structures, which would not be expected to follow the same relation as the incommensurable alloys, since the regions of the electron and hole Fermi surfaces connected by q are different. The incommensurable alloys fall fairly well on the line, except that

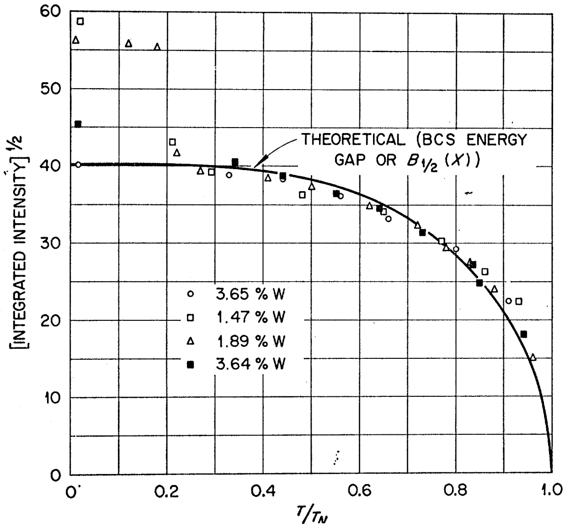

FIG. 10. The square root of the integrated intensity in a magnetic satellite versus reduced temperature for a number of Cr-W alloys. At low temperatures the intensity increases for some of the alloys because of a change in magnetic structure at the spin-flip temperature. The solid curve is calculated from the temperature dependence of the energy gap according to the BCS theory. This curve is indistinguishable from the Brillouin function of spin $\frac{1}{2}$.

the points for more concentrated Mo alloys are rather high and that for a 2.4% V alloy is decidedly low. The transport properties of the more concentrated V alloys are also anomalous and this point will be discussed further in II.

The temperature dependence of the moment and energy gap is predicted to follow the BCS[29] relation for the temperature dependence of the energy gap of a superconductor, as was first pointed out by Overhauser.[21] In Fig. 10 we have plotted the square root of the integrated intensity in a magnetic peak, which is proportional to the ordered moment, against the reduced temperature for several Cr-W alloys. The moments follow the BCS expression, within the experimental error if account is taken of the change in structure at the spin flip temperature. The BCS curve is, by a coincidence, remarkably close to the Brillouin function $B_{1/2}(T/T_N)$, and the results therefore also follow this function, but since the ordered moments are not localized at the Cr sites, and do not generally correspond to one unpaired spin per ion, this probably has no significance.

The rapid change in the Néel temperature and moment on alloying is one of the most striking features of this work. The Néel temperatures have been studied more extensively through transport property measurements and will be discussed in detail in II, but it is possible to make a number of qualitative deductions from the neutron-diffraction data. The rapid variation of T_N with electron concentration is immediately explained by the exponential dependence on λ, since a relatively small change in the electronic structure will be reflected in a large change in T_N, just as in a superconductor. In order to account for the change in T_N in terms of the electronic structure, it is necessary to consider a more realistic situation than the isotropic model. If the Fermi surfaces in the two bands interact over an area A and have a mean absolute separation t when one of them is displaced by q, then λ is proportional to[25]

$$[\gamma^2 V(0) A/\epsilon_F v] \ln(\pi/2t). \tag{5}$$

The variation of λ with t is relatively slow, so the most important effect of introducing a solute like V or Mn, which changes the electron concentration without greatly altering the form of the d wave functions, is to change the interaction area A. As may be seen from Fig. 7, the area of the hole octahedron exceeds that of the octahedral faces of the electron jack. The addition of Mn increases the volume of the jack while reducing that of the octahedron and, hence increases A, while V reduces A. The addition of V rapidly reduces the interaction area to the point where the antiferromagnetic state can no longer be sustained, while Mn increases T_N until the commensurable structure is reached, at which point the theory in this form no longer applies. The addition of Mo or W on the other hand probably modifies the Fermi surface only slightly, but since the d-wave functions are much less localized than those in Cr, the value of γ is reduced and T_N correspondingly falls. W is more potent than Mo as would be expected, since the $5d$ functions are less localized than the $4d$. When Re is added to Cr, the two effects compete. At first T_N rises and follows the Mn curve, but at higher concentrations the delocalization of the d functions causes it to drop rapidly to zero.

In pure Cr the longitudinal wave structure has the lowest energy at absolute zero, and this suggests that there exists an axial magnetic anisotropy in the tetragonal domains. As the temperature is increased, this anisotropy evidently decreases and the transverse wave becomes stable. The addition of any solute apparently decreases the axial anisotropy, so that the transverse structure rapidly becomes stable at all temperatures. Those solutes which most rapidly change the Néel temperature also have the greatest effect on the spin-flip temperature, but the reason for this and the details of the process are not understood.

The magnetic properties of Cr and its alloys are therefore explicable in terms of the model of Lomer,[24] as elaborated by Fedders and Martin.[25] In particular the temperature dependence of the moment, the linear relation between the Néel temperature and the moment, and the concentration dependence of the q vector, moment and Néel temperature are all qualitatively or semiquantitatively understood. The commensurable-incommensurable transition can be qualitatively explained, but the concentration dependence of the spin-flip temperature is not understood in detail. There are a number of striking parallels with the phenomenon of superconductivity, especially the appearance of an energy gap at the Fermi surface which depends exponentially on an interaction parameter and is linearly related to T_N. These matters will be discussed further in relation to the transport properties in II.

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[29] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).