Neutron-Diffraction Study of Cr and Cr Alloys

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The principle quantities which parameterize the antiferromagnetism of Cr are studied by neutron diffraction as a function of temperature, pressure, magnetic field, and concentration of solute atoms. In order to account for the observed intensities of the magnetic reflections, their dependence on magnetic field and temperature, the torque measurements of Montalvo and Marcus, and the creation of a "single-Q" state in field-cooling, a model is proposed based on the presumed existence of thermally active polarization domains within a "single-Q" region of the crystal. The variation of the polarization axis from place to place and with time lowers the free energy by an increase in entropy. The pressure dependence of the first-order phase change at 38.5°C is given as $dT_N/dP=-5.4$ deg/kbar. The temperature dependence of the length of the wave vector below T_N is given as $(1/Q)(dQ/dT)=6.3\times10^{-5}$ deg^{-1}. Alloys with 0.5 and 0.78 wt% Fe and with 0.9 wt% Co show a decrease in T_N of ~20°K per at.% of solute. The amplitudes of the magnetization waves increase and the wave vector Q approaches commensurateness with the lattice periodicity with increasing solute concentration in contrast to results for other solutes. Some unusual effects were observed for 2.3 wt% Fe samples.

THE number of "explained" properties of the antiferromagnetism of Cr seems to be fewer than the number of "unexplained" properties. In this paper we summarize our recent work[1-4] which may increase both numbers. Our neutron diffraction experiments consist of measurements of the principle quantities which parameterize the magnetization, that is M_Q, Q and **n** where

$$\mathbf{M}=M_Q\mathbf{n}\cos\mathbf{Q}\cdot\mathbf{r}. \quad (1)$$

The polarization axis **n** lies parallel to Q below 122°K, while above this "spin-flip" temperature T_{SF} it lies somewhere in the plane perpendicular to Q. We have det rmined how these quantities change with temperature[3] and also with concentration of the solutes Fe and Co.[4] In addition we have determined, within the limits of the magnetic fields available to us, the various effects of fields on the parameters of Eq. (1).

We interpret our results in terms of a model with two types of domain walls. One type, which we call Q walls, exists between two regions of the crystal with different directions for Q. The other type, which we call polarization walls, we assume to exist within a given single-Q domain. This latter type of wall must be absent below T_{SF}. The diffraction data may be analyzed to obtain the volumes V_{Q_i,n_i} which are the apparent volumes of the crystal with wave vector $\mathbf{Q}_i$ and polarization $\mathbf{n}_i$ where the i's refer to the three cubic axes. That is, above T_{SF} we determine not the direction of the polarization **n** but rather its components along the two cubic axes perpendicular to Q. As Q walls and polarization walls apparently move with changing temperature, one must observe six independent reflections above T_{SF} and three such spots below T_{SF} in order to obtain the true temperature dependence of M_Q. The magnetization vs temperature curves which we obtain lie markedly above the Brillouin functions.[3]

We have made preliminary diffraction studies of the effects of pressure. The first-order phase change[1] which occurs at 38.5°C at one atmosphere occurs 0.50°C lower at 92 atm. The transition is not so sharp under pressure, possibly because of inhomogeneous strain fields (see below). We can give an upper limit for $(1/Q)(dQ/dp)$ of 4×10^{-7} atm^{-1}. The change of Q with temperature at constant pressure[3] is $(1/Q)(dQ/dT)=6.3\times10^{-5}$ deg^{-1}. Our value of $dT_N/dP=-5.4$ deg/kbar is in agreement with the value deduced by Mitsui and Tomizuka[5] from resistivity measurements.

Our various measurements of the effects of field when a crystal is cooled through the 38.5°C transition, T_N, and when the field is applied at various temperatures below T_N have led us to propose a model for the structure of Cr above T_{SF} which stresses the contribution of spin wave excitations to the entropy. The excitations we envisage are variations of the polarization axis from place to place and with time in a single-Q region. A specific model, used for illustrative purposes, would be to assume that the number of polarization domains within a single-Q region is large and that **n**, while constant within each small polarization domain, varies from polarization domain to polarization domain in an uncorrelated manner. The number of walls could be limited by invoking a wall-wall interaction which increases the energy per wall when the walls become too close. The added entropy from the activation of

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[2] S. A. Werner, A. Arrott, and H. Kendrick, J. Appl. Phys. **37**, 1260 (1966).
[3] S. A. Werner, A. Arrott, and H. Kendrick, Phys. Rev. **155**, 496 (1967).
[4] A. Arrott, S. A. Werner, and H. Kendrick, Phys. Rev. (to to published).
[5] J. Mitsui and C. T. Tomizuka, Phys. Rev. **137**, 564 (1965).

the polarization degree of freedom would then make the single-Q domain containing many thermally excited polarization domains the stable state below T_N.

If a sufficiently large field is applied while a sample is cooled through T_N, the resulting single-Q crystal has Q parallel to the field H.[1] This would follow from the above model with the thermal activation of the polarization. The energy for a field applied parallel to Q is $-\frac{1}{2}\chi_\perp H^2V$ while for a field applied perpendicular to Q it is $-\frac{1}{2}\chi_\perp H^2V+\frac{1}{4}(\chi_\perp-\chi_{||})H^2V$. (This latter expression is a high-temperature approximation. The next term depends on the size of the domains, $1/kT$, and an anisotropy energy E_A.) This assumes that $\chi_\perp>\chi_{||}$, but this assumption by itself when applied to a model without the polarization contributions to the entropy does not account for the observed absence of domains with Q and n perpendicular to H.

We suppose that by invoking spin orbit coupling one could make a similar argument for the effect of strain fields in selecting a particular Q. Thus, in a crystal with inhomogeneous strain fields we would expect many Q type walls. But for either a uniform applied strain (tension)[6] or an applied magnetic field[1] of sufficient intensity, we would expect to achieve a single-Q state on cooling through T_N. The less inhomogeneous strain in a crystal, the more likely would it be for the crystal to be found in a single-Q state.[7]

If we apply a field perpendicular to Q in a single-Q crystal, we would expect the component of the polarization perpendicular to H and Q to increase while that parallel to H decreases and that the process should be reversible. This is precisely what we find for measurements in fields to 12 kG at 22°C.[3] Also if we apply 35 kG, the components of the polarization are the same before and after the application and removal of the field as long as we use a crystal prepared in a single-Q state. In such a state there is only slight preference of the polarization for one or the other of the two cubic axes perpendicular to Q.

While the application and removal of a 35 kG field will not affect a single-Q crystal, it will change the relative volumes of the crystal associated with each Q in a crystal with Q walls. This we interpret by saying that Q walls are more easily moved than they are nucleated.

Using the above model, we have calculated the torques which appear because of the anisotropy of the magnetic susceptibility. We are able to account for the field and temperature effects observed by Montalvo and Marcus.[8] We note that the extra entropy is present in the above model when n is free to choose directions in the plane perpendicular to Q, but it is absent when n is confined to the direction parallel to Q. It is possible that this entropy is the reason for the transition from longitudinal polarization to transverse polarization at T_{SF}.

We have studied pure Cr crystals (~80 mm³) prepared by vapor deposition in the reduction of chromium iodide and less pure Cr crystals (~50 mm³) mined out of polycrystalline ingots arc-melted in argon. The inhomogeneous strain fields are apparently larger in the latter crystals. The alloys on which we have taken neutron diffraction data were obtained also by the latter technique. We have obtained the magnetic structure and its temperature dependence in three Cr-rich Cr(Fe) alloys containing 0.5, 0.78 and 2.3 wt% Fe and one Cr(Co) alloy with 0.9 wt% Co.

The root-mean-square moment per atom was found to increase by 0.2 μ_B for 1% Fe in the Cr(Fe) alloys, which is considerably more moment than can be associated with the Fe atoms. The Néel temperature decreases ~20°K/1% Fe, while the spin-flip temperature decreases ~80°K/1% Fe. The wave vector increases toward commensurateness with the addition of Fe and shows a similar temperature dependence as observed in pure Cr. The magnetic structure was commensurate for the 2.3% Fe sample showing a first order phase change at the Néel temperature in agreement with measurements of bulk properties.[9]

The addition of 0.9% Co to Cr decreases the Néel point by 18°K. The moment is found to increase. No spin flip was observed down to 4.2°K.

As the temperature was decreased through the Néel point (260°K) in the 2.3% Fe sample, small satellite reflections were observed in addition to the (100) peak. As the temperature was lowered to 235°K, these satellite peaks disappeared leaving only a strong (100) reflection. A microprobe analysis of this sample showed that the Fe concentration varied from 1.8% to 2.8% over distances of 50 to 100 μ. It appears that regions of the crystal having lower Fe concentration have a higher Néel temperature and an incommensurate structure, and that when the regions of higher Fe concentration become antiferromagnetic, the choice of a commensurate magnetic structure is forced upon the crystal as a whole.

The result that the addition of either Fe or Co to Cr decreases the Néel temperature, while increasing the average moment and making the structure closer to commensurate is in direct contrast to the neutron diffraction results on Cr(Mn)[10] in which the moment increases as T_N increases and on Cr(V)[10] in which the moment decreases with a decrease in T_N. The structure becomes more nearly commensurate with the addition of Mn and goes further away from commensurate with the addition of V.

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