FIRST-ORDER MAGNETIC PHASE CHANGE IN CHROMIUM AT 38.5°C*

A. Arrott and S. A. Werner

Scientific Laboratory, Ford Motor Company, Dearborn, Michigan

and

H. Kendrick

Department of Nuclear Engineering, University of Michigan, Ann Arbor, Michigan

(Received 20 May 1965)

This note reports the properties of a very pure, near-perfect single crystal of chromium as revealed by neutron diffraction. The purity of this crystal and its degree of crystallographic perfection most likely account for our ability to observe two unique properties which have not been found in previous investigations of Cr.[1] The first is that Cr undergoes a first-order phase change at its "Néel temperature" of 38.5°C. The second is that the application of a magnetic field while the crystal is cooled through 38.5°C produces a magnetic structure which is described by a single wave vector parallel to the direction of the field during cooling. This structure is observed by neutron diffraction after the field is removed.

As has been often verified,[2] the magnetic structure of chromium is described by wave vectors

$$\vec{q} = 2\pi\vec{G} \pm \vec{Q}_i,$$

where the $\vec{G}$'s are the reciprocal lattice vectors and the $\vec{Q}_i$'s are wave vectors along the three cubic axes $\hat{x}_i$. The magnitude of the wave vector $\vec{Q}_i$ is slightly temperature dependent and remains close to, but not equal to, $2\pi/a$. Thus the possible magnetic reflections are in groups of six about the positions $\vec{q} = 2\pi\vec{G} \pm (2\pi/a)\hat{x}_i$. The polarizations associated with the wave vectors $\vec{Q}_i$ are transverse above 115°K and longitudinal below 115°K. The first-order phase change at 115°K is called the "spin-flip" temperature.

The crystals studied here are formed by vapor deposition in the reduction of chromium iodide, a commercial process. The best crystal, selected from several kilograms of small crystals, shows a very narrow mosaic spread (less than 0.001 rad). The volume of this crystal is approximately 100 mm^3. This crystal has been cooled many times from 50 to 30°C, sometimes in a magnetic field of 40 kG and sometimes not. From the intensities of the 36 magnetic reflections closest to the origin of reciprocal lattice space, we conclude that this crystal is characterized by longitudinally polarized waves $\vec{Q}_i$ below the spin-flip temperature and by transversely polarized waves $\vec{Q}_i$ above the spin-flip temperature. When cooled in the absence of an applied field, the three wave vectors $\vec{Q}_i$ are equally represented. When cooled through 38.5°C with 40 kG along, say, the $\hat{x}_2$ axis, only the wave vector $\vec{Q}_2$ is represented. We call this field-cooled state a "single-$\vec{Q}$" state. Such a state is specified by $\pm(2\pi/a)(1,\pm\epsilon,0)$ and $\pm(2\pi/a)(0,\pm\epsilon,1)$ reflections, and only these reflections, below the spin-flip temperature; while above only the additional reflections $\pm(2\pi/a)(0,1\pm\epsilon,0)$ appear. We introduce the parameter ϵ only for convenience of notation. For instance, $(2\pi/a)(0,1-\epsilon,0)$ is $\vec{Q}_2$, the reflection $(2\pi/a)(1,\epsilon,0)$ is $(2\pi/a)(1,1,0) -\vec{Q}_2$. Below the spin-flip temperature the polarization of this "single-$\vec{Q}$" crystal is longitudinal. Above the spin-flip temperature the polarization is transverse.

When cooled through 38.5°C in nominally zero field, the crystal is magnetically cubic. That is, the reflections $\vec{q} = \vec{Q}_1$, $\vec{Q}_2$, and $\vec{Q}_3$ have equal intensity. However, the other magnetic reflections do not have equal intensity, indicating that the transverse polarization vectors have preferential orientation. Application and removal of a magnetic field of 40 kG at 30°C produces a state which is neither "single-$\vec{Q}$" nor "apparently cubic." The "preferred $\vec{Q}$" is parallel to the field. The polarizations of the "unpreferred $\vec{Q}$'s" surprisingly are preferentially aligned parallel to the field.

Magnetic states exhibiting more than one $\vec{Q}$ cannot be interpreted unambiguously. For example, the "apparently cubic" state may in fact be a "triple-$\vec{Q}$" state with three equal-amplitude $\vec{Q}$'s coexisting in every region of the crystal. Or it may be a multidomain configuration with each domain being in a "single-

$\vec{Q}$" state. One would hope that a "single-$\vec{Q}$" state would, because of its tetragonal symmetry, produce a measurable tetragonal distortion of the crystal. This would allow the foregoing alternatives to be distinguished. Weiss[4] has performed an x-ray experiment on a single crystal which did not show any line broadening below the Néel temperature. Unfortunately, his conclusion that the triple-$\vec{Q}$ alternative was indicated presumed that single-$\vec{Q}$ domains would have tetragonal distortions, and that the observed region of the crystal would have comprised many such domains. We are carrying out x-ray experiments on the "single-$\vec{Q}$" and the "apparently cubic" states of our crystal.

From studies of the temperature dependence of the magnetic reflections of this crystal in the "single-$\vec{Q}$" condition and in several "non-single-$\vec{Q}$" conditions, we find a sudden disappearance of the magnetic reflections at 38.5°C. For the "single-$\vec{Q}$" state, the amplitude of the $\vec{Q}_2$ magnetization wave (found by comparison with the nuclear reflections) is ~500 G (equivalent to point dipoles of strength 0.6 μ_B) just above the spin-flip temperature. The amplitude decreases only to ~175 G (35% of its low temperature value) at 38.4°C before it abruptly drops to zero. Above 38.5°C all trace of the magnetic peaks are gone except for a very weak and broad background of magnetic scattering centered about the positions $\pm(2\pi/a)(1,0,0)$, $\pm(2\pi/a)(0,1,0)$, $\pm(2\pi/a)(0,0,1)$. Just reaching the Néel temperature is sufficient to destroy the "single-$\vec{Q}$" character of the crystal. To recover that property the field cooling process must be repeated. We are at present studying the field requirements for changing the $\vec{Q}$ character and the polarization of this Cr crystal.

Some of the experimental details are as follows: Our monochromating crystal is a 2.5-cm×2.5-cm×8-cm bar of silicon used in transmission. The 111 spacing of silicon is a close match to the 100 spacing of Cr. Thus we work nearly in the "parallel" position. This enables us to get very sharp crystal-rocking curves with a divergent incident beam and a "wide-open" counter. In particular, with a beam having an angular divergence of about 0.02 rad and with the circular cross-section counter accepting the large solid angle of 0.01 sr, the width of the magnetic reflection is less than 0.002 rad. Thus with fixed counter position, a crystal rotation through the nominal position $(2\pi/a)(0,1,0)$ shows seven reflections: $(2\pi/$

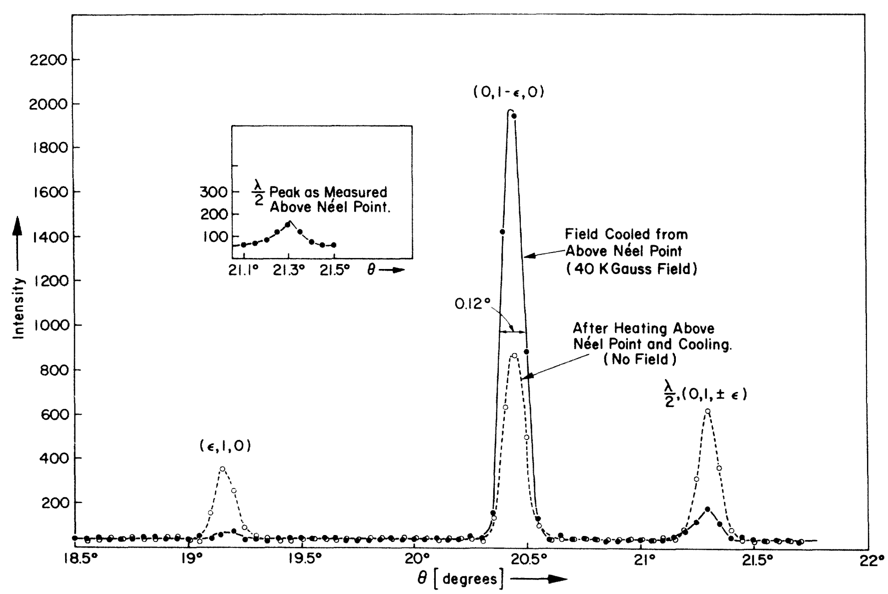

FIG. 1. The intensity of magnetic reflections at 29.6°C after cooling in 40 kG from 50 to 30°C and removing the field is compared to the intensity of magnetic reflections after the sample was subsequently raised to 40°C and cooled in the absence of an applied magnetic field. The field was applied in the (0, 1, 0) direction. The data show the magnetic reflections $(2\pi/a)(1,1,0)-\vec{Q}_1$ which is labeled $(\epsilon,1,0)$, the principle vector $\vec{Q}_2$ which is labeled $(0,1-\epsilon,0)$, and the combined reflection of the "$\lambda/2$" contamination (shown separately in the inset for above 40°C), $(2\pi/a)(0,1,1)-\vec{Q}_3=(2\pi/a)(0,1,\epsilon)$ and $(2\pi/a)(0,1,-1)-\vec{Q}_3=(2\pi/a)(0,1,-\epsilon)$.

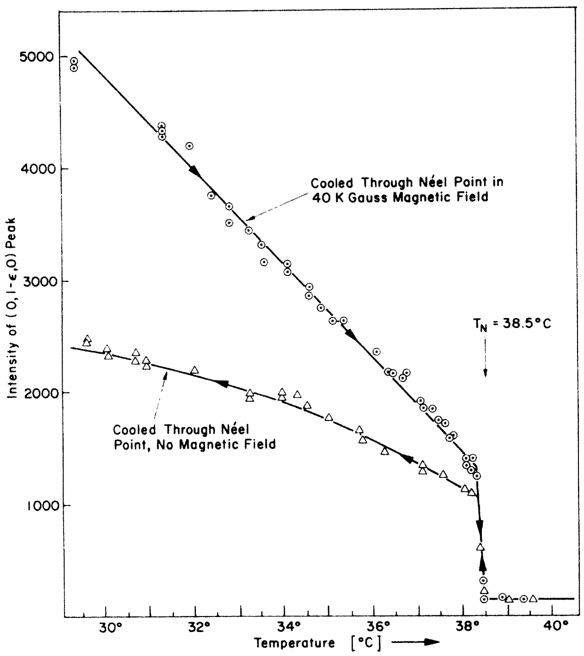

FIG. 2. The temperature dependence of the magnetic reflection $q = Q_2 = (2\pi/a)(0, 1-\epsilon, 0)$ from 29 to 40°C and back to 29°C for a sample initially in the "single-$\vec{Q}$" state [as a result of applying a field in the (0, 1, 0) direction while cooling from 50 to 30°C].

$a)(\epsilon, 1, 0)$, $(2\pi/a)(0, 1-\epsilon, 0)$, $(2\pi/a)(0, 1, \epsilon)$, "$\lambda/2$," and $(2\pi/a)(0, 1, -\epsilon)$, $(2\pi/a)(0, 1+\epsilon, 0)$, and $(2\pi/a)(-\epsilon, 1, 0)$ in that order if the (0, 0, 1) axis is not quite vertical. If the (0, 0, 1) axis is vertical, the three peaks $(2\pi/a)(0, 1, \epsilon)$, "$\lambda/2$," and $(2\pi/a)(0, 1, -\epsilon)$ are superimposed. The "$\lambda/2$" contribution ($\lambda = 2.095$ Å) would be absent from silicon, were it not for multiple reflections. The inset of Fig. 1 shows this contribution. Figure 1 shows part of a crystal-rocking curve through the (0, 1, 0) position for the field-cooled sample. The corresponding curve after excursion to 40°C is also shown. The temperature dependence of the peak intensity of the $\vec{q} = \vec{Q}_2 = (2\pi/a)(0, 1-\epsilon, 0)$ reflection is shown in Fig. 2. The sharp drop-off is more striking than the curve indicates, and has been reproduced several times. One can observe the scaler suddenly stop counting at "constant" temperature during a cycle of the temperature controller. The temperature of the transition (as determined by a platinum resistance thermometer in an isothermal enclosure with the crystal) is reproducible to better than 0.05°C. The sharp transition is observed for other states of the crystal as well as for the "single-$\vec{Q}$" state.

The relation of our findings to the work of Montalvo and Marcus[5] on the magnetic anisotropy produced by similar field-cooling experiments, and studied by torque magnetometer and de Haas–van Alphen measurements, should lead to a more complete understanding of the magnetic phenomena in chromium.

The authors wish to acknowledge valuable discussions with Dr. A. W. Overhauser and Dr. H. Sato, and the help of Professor J. S. King in establishing the experimental facilities.

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*Neutron diffraction work performed at the Ford Nuclear Reactor, Phoenix Memorial Laboratory, University of Michigan, Ann Arbor, Michigan.

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[2]In addition to reference 1, see L. Corliss, J. Hastings, and R. Weiss, Phys. Rev. Letters 3, 211 (1959); V. N. Bykov, V. S. Golovkin, N. V. Ageev, V. A. Lerdik, and S. I. Vinogradov, Dokl. Akad. Nauk SSSR 128, 1153 (1959) [translation: Soviet Phys.—Doklady 4, 1070 (1960); J. M. Hastings, Bull. Am. Phys. Soc. 5, 455 (1960); M. K. Wilkinson, E. O. Wollan, and W. C. Koehler, Bull. Am. Phys. Soc. 5, 456 (1960).

[3]An experiment suggested by A. W. Overhauser and A. Arrott, Phys. Rev. Letters 4, 226 (1960).

[4]R. J. Weiss, Phys. Letters 10, 45 (1964). See also M. E. Straumannis and C. C. Weng, Acta Cryst. 8, 367 (1955).

[5]A. A. Montalvo and J. A. Marcus, Phys. Letters 8, 151 (1964).