Temperature and Magnetic-Field Dependence of the Antiferromagnetism in Pure Chromium*

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The results of neutron-diffraction experiments on the temperature and magnetic-field dependence of the antiferromagnetism in pure chromium are presented. A comparison with previously published temperature-dependence data is given. Temperature hysteresis is generally observed due to the temperature dependence of the magnetic domain structure. Relatively small magnetic fields are found to be sufficient to rotate the polarization associated with a given wave vector. A simple model is proposed, based on thermal fluctuations of polarization of the antiferromagnetic domains as a whole, which explains the magnetic-field effects found in this study and the torque-magnetometer measurements of Montalvo and Marcus. This model accounts for effects on chromium of cooling in a magnetic field.

I. INTRODUCTION

THE purpose of this paper is to report the results of some neutron diffraction experiments on the temperature and magnetic field dependence of the antiferromagnetism in pure chromium. We have examined a number of single crystals of chromium; detailed results of experiments on just two of these crystals are reported here. The first sample (Cr-1) was grown from the vapor in the reduction of chromium iodide and is a highly perfect single crystal. The volume of this crystal is 83 mm^3, and its mosaic spread parameter has been estimated to be about $\frac{1}{2}$ min, as revealed by a rocking curve using a Si (111) monochromator [which places the magnetic reflections about the (100) in very nearly the parallel position]. Preliminary results on this crystal have been reported previously.[1,2] The second sample (Cr-2) was mined out of a large-grained ingot of arc-melted chromium.[3] The volume of this sample is 44 mm^3 and its mosaic width is about 10 min. Both of these samples show a first-order phase transformation at the Néel point (38.5°C).

We wish to call attention to two particular results. The first is that the magnetic reflections in chromium will, in general, show temperature hysteresis. An interpretation of this result which is consistent with all our experimental data is that [above the spin-flip temperature (122°K)] the magnetic structure of chromium is described by a linear, transverse static magnetization wave in each of six types of magnetic domains. That is, a given domain contains a fundamental magnetization wave with its wave vector $\mathbf{Q}$ along a cube axis and its polarization pointing along one of the other two cubic axes.[4] There are six independent possible choices for domains of this type. As the temperature of the sample is changed, the fractional volume occupied by a domain of a given type may also change, perhaps as a result of strain fields. Consequently the various magnetic reflections in chromium show different temperature dependences, and it is necessary to observe six independent reflections in order to obtain the true temperature dependence of the amplitude of the magnetization waves. The thermal hysteresis observed for a particular magnetic reflection is due to the temperature dependence of the fractional volume of the crystal contributing to the reflection.

The second observation is that the "average" direction of polarization associated with waves of a given $\mathbf{Q}$ vector can be rotated by applying a magnetic field perpendicular to $\mathbf{Q}$. This "rotation effect" is completely reversible for fields up to 12.4 kG. The experimental results do not allow a choice to be made for the mechanism involved in this effect. There are two possibilities: (a) the average direction of polarization within a given domain is rotated away from a cubic axis as a continuous function of applied field, or (b) the domains having their polarization parallel to the applied field switch to being domains with polarization perpendicular to the applied field, possibly through domain-wall motion.

As has often been verified, the magnetic reflections in chromium can be described by the set of scattering vectors

$$\mathbf{q}=2\pi\mathbf{G}\pm\mathbf{Q}_i, \qquad (1)$$

where the $\mathbf{G}$'s are the reciprocal lattice vectors and the $\mathbf{Q}_i$'s are the fundamental wave vectors along the three cubic axes $\hat{x}_i$. $\mathbf{Q}_i$ is slightly temperature-dependent, and is close to but not equal to $2\pi/a$. See Fig. 1. Therefore,

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

[1] A. Arrott, S. A. Werner, and H. Kendrick, Phys. Rev. Letters 14, 1024 (1965).

[2] S. A. Werner, A. Arrott, and H. Kendrick, J. Appl. Phys. 37, 1260 (1966).

[3] This ingot was prepared by Materials Research Corporation, Orangeburg, New York.

[4] In the discussion part of this paper it is suggested that the polarization direction of a given domain may fluctuate about the cubic axes because of thermal excitations.

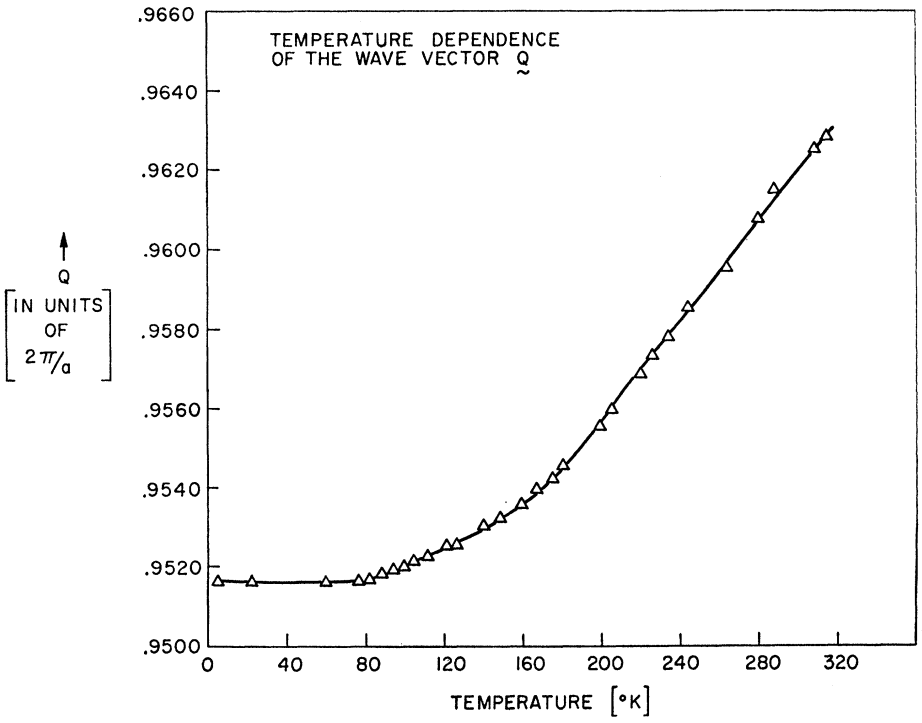

FIG. 1. The temperature dependence of the wave vector **Q** as a function of temperature for pure chromium. These data were taken on Cr-1 and agree very well with the data of Shirane and Takei. The precision in measuring ϵ was better than 1 part in 300.

there are six possible reflections about each of the positions $\mathbf{q}=2\pi\mathbf{G}\pm(2\pi/a)\hat{x}_i$. We denote the distance away from $2\pi\mathbf{G}\pm(2\pi/a)\hat{x}_i$ in reciprocal lattice space that these reflections occur by ϵ. The polarizations associated with the wave vectors $\mathbf{Q}_i$ are transverse above the spin-flip temperature (122°K) and longitudinal below. The work reported here is based on the observation of (the reflections forming) the "jack" centered at the three (100)-type positions.

The temperature dependence of the amplitude of the magnetization waves in chromium has been given by a number of authors[5–8] on a variety of samples. A comparison of several of these results is shown in Fig. 2. Obviously there is lack of agreement among these curves. On the basis of Bacon's data[6] on two polycrystalline samples of different grain size and the powder data of Wilkinson *et al.*,[7] it appears that the early suggestion that strains are responsible for smearing out the observed phase transformation at the Néel point is reasonable. The effects of applying a stress while cooling through the Néel point have been reported by Bastow and Street.[9] It seems likely that observation of the abrupt change in the magnetic reflections at the Néel point is contingent upon having a relatively strain-free crystal.

The data given by Shirane and Takei[8] on the $(1,\epsilon,0)$ reflection are considerably lower than all the other temperature dependence curves reported previously. However, the curve does show a very distinct Néel point. As will be seen in the next section, a reasonable explanation for the shape of that observed intensity curve is that the fractional volume of the crystal contributing to the $(1,\epsilon,0)$ reflection was decreasing as the temperature was increased.

The curve shown in Fig. 2 due to Bykov *et al.*[5] was obtained on heating. The data obtained on cooling (not shown) were considerably lower, indicating temperature hysteresis. This type of behavior is evidently due to a repopulation of the various types of domains as a function of temperature. However, Bykov *et al.* give a spin-flip temperature of 148°K. We have obtained a spin-flip temperature of ~122°K in all of the crystals we have examined, which is in agreement with the temperature given by Shirane and Takei. This discrepancy remains a mystery, and cannot be resolved on the basis of various degrees of strain which may be present in different samples. The higher spin-flip temperature observed by Bykov cannot be explained on the basis of impurities since the results reported by Koehler *et al.*[10] for several alloys show a decrease in T_{SF}. We have found that the temperature width over which the spins

[5] V. N. Bykov, V. S. Golovkin, N. V. Ageev, V. A. Lerdik, and S. I. Vinogradov, Dokl. Akad. Nauk SSSR **128**, 1128 (1959) [English transl.: Soviet Phys.—Doklady **4**, 1070 (1960)].
[6] G. E. Bacon, Acta Cryst. **14**, 823 (1961).
[7] M. K. Wilkinson, E. O. Wollan, W. C. Koehler, and J. W. Cable, Phys. Rev. **127**, 2080 (1962).
[8] G. Shirane and W. J. Takei, J. Phys. Soc. Japan Suppl. B-III **17**, 35 (1962).
[9] T. J. Bastow and R. Street, Phys. Rev. **141**, 510 (1966).
[10] W. C. Koehler, R. M. Moon, A. L. Trego, A. R. Mackintosh, J. Appl. Phys. **37**, 1259 (1966); Phys. Rev. **151**, 425 (1966).

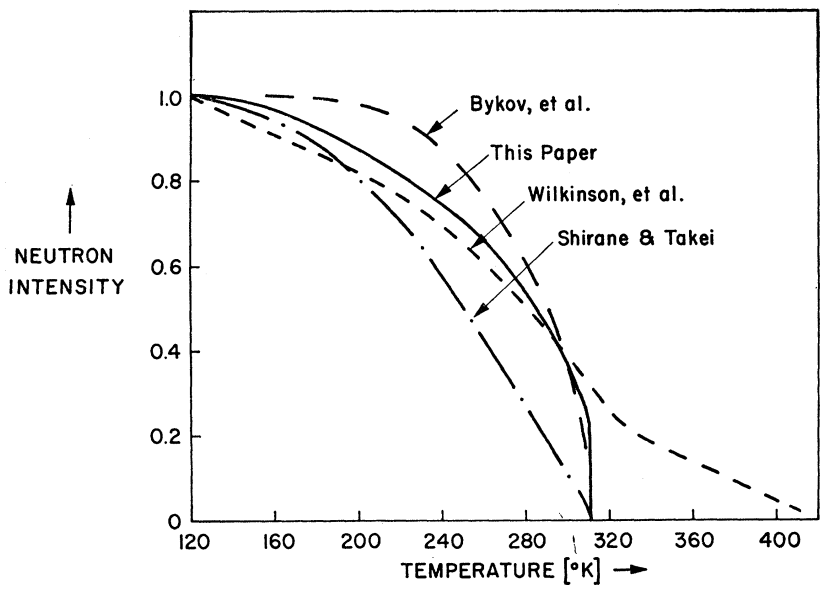

FIG. 2. A comparison of various temperature-dependence curves reported on pure chromium.

flip varies from about 1°K in a crystal grown from the vapor to about 10°K in an arc-melted sample. These samples undoubtedly have different strain fields. The upper edge of this temperature width is consistently ~122°K, and does not reflect the past thermal history of the sample.

II. TEMPERATURE DEPENDENCE OF M_Q

A. Domains

In the absence of both primary and secondary extinction the integrated intensity corresponding to a particular Fourier component of the magnetization $\mathbf{M}_\mathbf{q}$ is

$$I(\mathbf{q})=AM_\mathbf{q}^2(T)V_{M_q}(T)(\sin^2\theta_{M_q,\mathbf{q}})[\lambda^3/\sin 2\theta_B], \quad (2)$$

where V_{M_q} is the volume of the crystal occupied by domains having a nonzero Fourier component $\mathbf{M}_\mathbf{q}$, $\theta_{M_q,\mathbf{q}}$ is the angle between the scattering vector $\mathbf{q}$ and the direction of $\mathbf{M}_\mathbf{q}$, λ is the neutron wavelength, $2\theta_B$ is the scattering angle, and A is a constant independent of λ, q, and $\mathbf{M}_\mathbf{q}$. It has not been established that the preferred direction of $\mathbf{M}_\mathbf{q}$ is one of the three cubic axes in the body-centered cubic lattice of chromium, although all of our experimental data are consistent with this model. The wave vector $\mathbf{Q}$ of the linear magnetization wave definitely does lie along a cubic axis. In general both $\mathbf{M}_\mathbf{q}^2$ and V_{M_q} will depend on the temperature T. Table I gives the intensity expected at each of the six reflections close to the (100) position. The two subscripts $(\mathbf{Q}_i,\eta_j)$ denote the propagation vector of the fundamental wave and its polarization direction; that is, $V_{M_q}=V_{\mathbf{Q}_i,\eta_j}$ where $\mathbf{q}$ is defined by Eq. (1) and $\boldsymbol{\eta}_j$ is the direction of $\mathbf{M}_\mathbf{q}$. The coefficients B_i are defined by

$$B_1=A\frac{\lambda^3}{\sin 2\theta_{(1-\epsilon,0,0)}},$$
$$B_2=A\frac{\lambda^3}{\sin 2\theta_{(1,\epsilon,0)}}, \quad (3)$$
$$B_3=A\frac{\lambda^3}{\sin 2\theta_{(1+\epsilon,0,0)}}.$$

Expressions for the reflections about (010) and (001) can be written down in a similar manner. It is reasonable to assume that the temperature dependence of $M_\mathbf{q}^2$ is independent of $\mathbf{q}$. The magnetic form factor [11] $f(\mathbf{q})$ can be used to scale the various Fourier components. We assume $f(\mathbf{q})$ is independent of temperature. We have verified that the ratio

$$I(1+\epsilon,0,0)/I(1-\epsilon,0,0)=0.78\pm0.02,$$

independent of temperature. On a rigid spin model[12] (which appears to be appropriate for chromium), the form factor depends on $\mathbf{q}$ and not on the reciprocal

TABLE I. Theoretical formulas for reflection intensities near (100) above the spin-flip threshold.

$I(1,\epsilon,0)$	$=B_2(M_{2\pi\mathbf{G}_{110}-\mathbf{Q}_2,\eta_3})^2V_{\mathbf{Q}_2,\eta_3}$
$I(1,-\epsilon,0)$	$=B_2(M_{2\pi\mathbf{G}_{1\bar{1}0}+\mathbf{Q}_2,\eta_3})^2V_{\mathbf{Q}_2,\eta_3}$
$I(1,0,\epsilon)$	$=B_2(M_{2\pi\mathbf{G}_{101}-\mathbf{Q}_3,\eta_2})^2V_{\mathbf{Q}_3,\eta_2}$
$I(1,0,-\epsilon)$	$=B_2(M_{2\pi\mathbf{G}_{10\bar{1}}+\mathbf{Q}_3,\eta_2})^2V_{\mathbf{Q}_3,\eta_2}$
$I(1-\epsilon,0,0)$	$=B_1[M_{\mathbf{Q}_1,\eta_2}{}^2V_{\mathbf{Q}_1,\eta_2}+M_{\mathbf{Q}_1,\eta_3}{}^2V_{\mathbf{Q}_1,\eta_3}]$
$I(1+\epsilon,0,0)$	$=B_3[(M_{2\pi\mathbf{G}_{200}-\mathbf{Q}_1,\eta_2})^2V_{\mathbf{Q}_1,\eta_2}+(M_{2\pi\mathbf{G}_{200}-\mathbf{Q}_1,\eta_3})^2V_{\mathbf{Q}_1,\eta_3}]$.

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

[12] See A. Arrott, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. IIB.

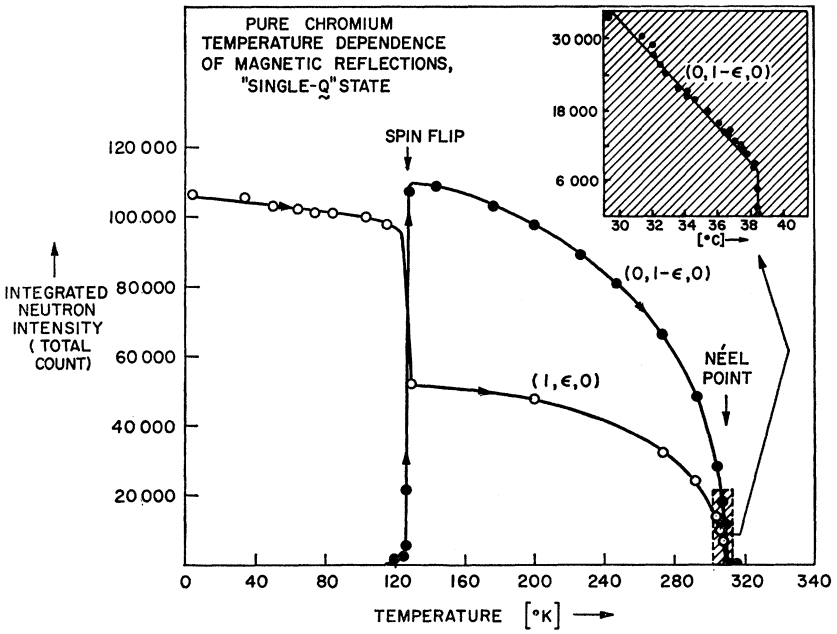

FIG. 3. Temperature dependence of the magnetic reflections in Cr-1 in the "single-Q" state.

lattice vector $\mathbf{G}$ in Eq. (1) as it would in a flexible spin model. We assume that f^2 varies linearly with $|\mathbf{q}|$ near $|\mathbf{q}|=2\pi/a$.

B. "Single-Q" State

Figure 3 shows the temperature dependence of the $(0, 1-\epsilon, 0)$ and $(1,\epsilon,0)$ reflection in Cr-1 when the crystal is in a "single-Q" state.[1] There are only two types of domains in this case above the spin-flip temperature, specified by the volumes $V_{\mathbf{Q}_2,\eta_1}$ and $V_{\mathbf{Q}_2,\eta_3}$, and only one type of domain, specified by $V_{\mathbf{Q}_2,\eta_2}$ below the spin flip. Consequently, if V_0 denotes the total volume of the crystal, we must have

$$\begin{aligned}&\text{above spin flip: } V_{\mathbf{Q}_2,\eta_1}+V_{\mathbf{Q}_2,\eta_3}=V_0\\&\text{below spin flip: } V_{\mathbf{Q}_2,\eta_2}=V_0 \qquad \text{"single-}Q\text{" state,}\end{aligned} \tag{4}$$

and since $M_{\mathbf{Q}_2,\eta_1}{}^2=M_{\mathbf{Q}_2,\eta_3}{}^2$, a measurement of the temperature dependence of $I(0, 1-\epsilon, 0)$ in the "single-Q" state gives the temperature dependence of the amplitude of the magnetization wave of wave vector $\mathbf{Q}_2$ directly. It is interesting to note that once a crystal is put in the "single-Q" state, it remains "single-Q" independent of temperature as long as the temperature does not go above the first-order phase transformation at the Néel point. If one normalizes the data of the $(1,\epsilon,0)$ reflection to the $(0, 1-\epsilon, 0)$ reflection in this case, the points lie precisely on the same curve. This says that the fractional volume of the crystal occupied by domains of each transverse polarization does not change with temperature when the crystal is in a "single-Q" state.

Since Cr-1 is a highly perfect crystal, we have been concerned about whether the magnetic reflections are affected by some extinction. The nuclear reflections clearly are affected by extinction. However, even in the "single-Q" state the magnetic reflections are down by a factor of about 10 from the nuclear peaks. In order to check this, the same temperature dependence was measured using neutrons of about one-half the wavelength. Experimentally this is achieved by reorienting our Si monochromating crystal. The scattering angle from the monochromator is set at 40°. Using the (111) reflection in Si, we obtain a beam of 2.09 Å neutrons at this angle with negligible second-order contamination. By reorienting the Si monochromating crystal with its remote controls, we utilize the (311) reflection to produce a 1.07 Å neutron beam. [The second-order contamination in this beam is negligible since the structure factor for (622) in Si is zero.] This change of wavelength decreases the probability for Bragg scattering per unit path for the magnetic reflections about the (100) by a factor of ~ 4 (in the absence of primary extinction). This reduction in wavelength also reduces the effects of primary extinction.

These two temperature dependence curves were normalized to 1.0 at 128°K (just above the spin flip). These results are compared in Fig. 4. The 1.07 Å data fall slightly below (maximum deviation $\sim 5\%$) the 2.09 Å data indicating that a small amount of extinction is probably present in the magnetic reflections taken with the longer wavelength.

C. "Multi-Q" State

Figure 5 shows the temperature dependence of the $(1-\epsilon, 0,0)$ reflection in Cr-1 when the crystal was initially in a "multi-Q" state. The sample was cooled down to 128°K and data were taken on the six magnetic

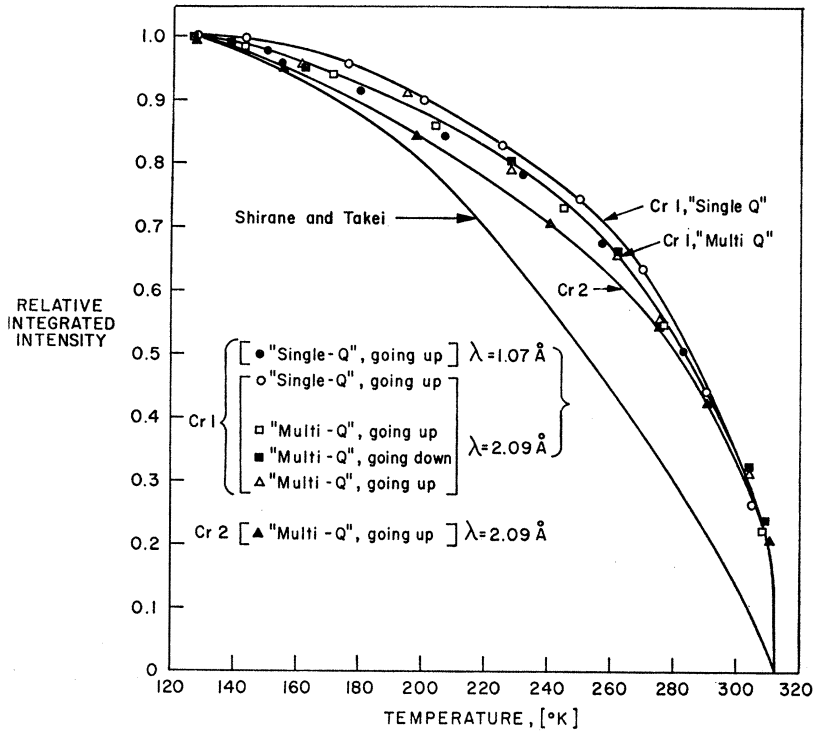

FIG. 4. Comparison of data taken on Cr-1 and Cr-2. All data have been normalized to 1.0 at 128°K (just above the spin-flip temperature). The curve given by Shirane and Takei follows a Brillouin function ($B_{1/2}$) very closely. (This curve is also very close to the temperature dependence of the energy gap in the BCS theory of superconductivity.)

reflections about both the (100) and (010) positions as a function of temperature. Only the results for the $(1-\epsilon, 0,0)$ reflection are shown here. Curve 1 was taken on heating. The sample was heated a few degrees above the Néel point T_N, and then the points on curve 2 were obtained on cooling back to 128°K. Curve 3 was obtained on heating a second time to a point a few degrees below T_N, and subsequently, curve 4 was obtained on cooling. All of the other reflections also exhibit temperature hysteresis.

If the origin of this temperature hysteresis is that the volume of domains contributing to a particular reflection is changing with temperature, one would expect that the sum of an appropriate choice of six independent reflections should show no thermal hysteresis. Since each $(1,\epsilon,0)$-type reflection is due to a single type of domain, by adding $I(1,\epsilon,0)+I(1,0,\epsilon)+I(0,1,\epsilon)+I(\epsilon,1,0)+I(\epsilon,0,1)+I(0,\epsilon,1)$ we have a total intensity J which is directly proportional to the squared amplitude of the magnetization wave, and independent of the temperature variation of the volumes of the individual domains. The same number is obtained by forming the following sum:

$$J=\tfrac{1}{2}[I(1-\epsilon, 0,0)+I(1+\epsilon, 0,0)+I(0, 1-\epsilon, 0)+I(0, 1+\epsilon, 0)]+I(1,0,\epsilon)+I(0,1,\epsilon)$$
$$=B_2M_0^2(T)V_0, \qquad (5)$$

where we have defined M_0 as the amplitude of the fundamental magnetization wave normalized to $\mathbf{q}=(2\pi/a)(1,0,0)$. This second procedure proved to be somewhat easier because all of the reflections in Eq. (5) could be seen keeping the cubic axis (001) vertical.

Figure 4 shows the results of these experiments where the data have again been normalized to 1.0 at 128°K. The lack of any temperature hysteresis in this result supports the model in which the volumes occupied by the six types of domains are changing with temperature. These experiments were done with 2.09 Å neutrons. Since each reflection is down by a factor of about 3 from the equivalent nonzero reflections in the "single-Q"

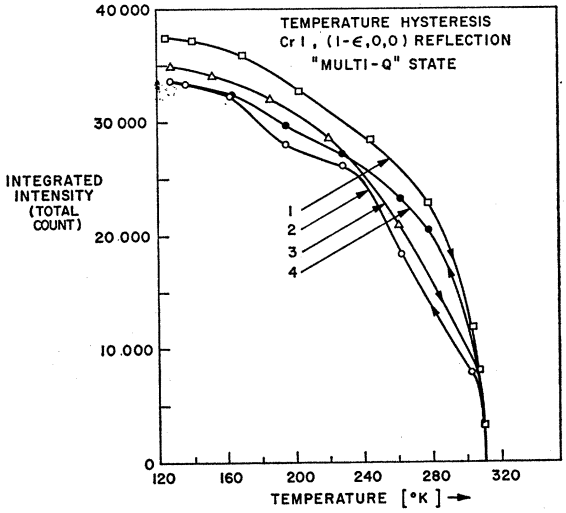

FIG. 5. These curves show the temperature hysteresis observed on the $(1-\epsilon, 0,0)$ reflection in pure chromium (Cr-1).

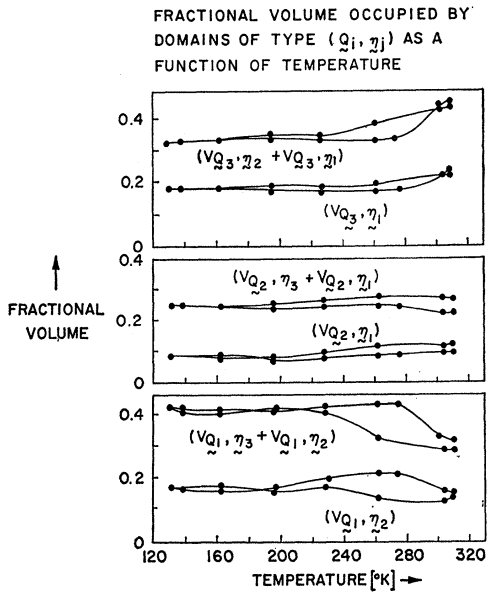

FIG. 6. Temperature dependence of the fractional volumes occupied by each of the six types of antiferromagnetic domains existing about the spin-flip temperature.

state, we would expect the effect of extinction to be less in the "multi-Q" state. This, in fact, appears to be the case, since the measured temperature dependence $M_0^2(T)$ obtained here follows the 1.07 Å, "single-Q" data more closely than the 2.09 Å "single-Q" curve of Fig. 3.

Since we now have the magnetization as a function of temperature $M_0^2(T)$, we can divide the measured intensities by this function and obtain the actual temperature dependence of the volumes $V_{\mathbf{Q}_i,\boldsymbol{\eta}_j}$ occupied by each of the six types of domains. We have done this and the resulting hysteresis effects are shown in Fig. 6. Note that there are various processes by which a repopulation of the domain structure can occur. For example, the polarization within a given domain can simply rotate about $\mathbf{Q}_i$:

$$(\mathbf{Q}_i,\boldsymbol{\eta}_j) \rightarrow (\mathbf{Q}_i,\boldsymbol{\eta}_k),$$

or the direction of polarization may remain the same with a switch in the direction of the wave vector:

$$(\mathbf{Q}_i,\boldsymbol{\eta}_k) \rightarrow (\mathbf{Q}_j,\boldsymbol{\eta}_k).$$

We call the boundary between two regions in which the wave vector $\mathbf{Q}$ is the same, yet the polarization is different, a "polarization wall." A "Q-switch" wall is one for which the $\mathbf{Q}$ vector changes direction. Whether an entire domain changes all at once, or whether the process is better described by gradual domain-wall motion is not known. (See Sec. IV.)

In any case, the magnetic state of chromium below the Néel point contains various antiferromagnetic domain structures which are dependent upon temperature and the past thermal and magnetic history of the sample. The details of the types of domain walls and their motion is an interesting (and probably very difficult) research problem by itself.

D. Crystals Grown by Arc Melting (Cr-2)

As a further experiment on the temperature dependence of the magnetization waves in chromium, we examined the magnetic reflections about the (100) and (010) in a crystal grown by arc melting. By forming the sum given by Eq. (5), the squared amplitude of the magnetization wave in this crystal was obtained. These numbers are shown as the curve labeled Cr-2 in Fig. 4. Although these data lie considerably above the curve given by Shirane and Takei, it is nevertheless lower than the data obtained on Cr-1. There are two possible xeplanations for this: extinction, or strain. Since this sample was about $\frac{1}{2}$ the size of Cr-1 and about 20 times broader in mosaic structure, the effect of secondary extinction would be expected to be less. However, in view of the small change noted in the data on Cr-1 upon changing wavelength by a factor of 2, it seems most probable that this difference is due to the larger strain expected in an arc-melted sample, especially in view of the fact that this sample was mined out of a larger ingot by spark cutting and subsequently polished to remove small subsidiary gains.

We would like to conclude that the temperature curve $M_0^2(T)$ given in Fig. 4 for Cr-1 is in fact the correct dependence on temperature for a highly pure, strain-free sample of chromium. Considerable effort has been expended to make a convincing experimental argument for the lack of important extinction effects in obtaining these data. However, there may still be some question on this matter.[13]

We should also point out that the temperature hysteresis observed in this second sample, Cr-2, is significantly less than in Cr-1. Apparently, strains have the effect of stabilizing a particular domain structure.

III. MAGNETIC-FIELD EFFECTS

In two earlier papers[1,2] we discussed the effects of large magnetic fields on the structure of chromium. Two significant results were given:

(1) Cooling Cr-1 through the Néel point in the presence of fields greater than about 24 kG produces a magnetic structure described by a single $\mathbf{Q}$ vector

[13] There are a number of additional arguments which we can advance for the lack of extinction on the magnetic peaks in both of these crystals. In particular, normalizing the magnetic reflections to the (200) reflections in Cr-2 gives a root-mean-square moment per chromium atom of 0.43 μB in good agreement with previous measurements. This requires that there is also no extinction on the nuclear reflection (200) in this sample. The ratio $I(1+\epsilon,0,0)/I(1-\epsilon,0,0)=0.78\pm0.02$ at all temperatures above T_{SF} for both samples. Consequently, one must conclude that if there is no extinction in Cr-2, there must also be no extinction in Cr-1; otherwise this ratio would be larger in Cr-1.

parallel to the applied field if the applied field is parallel to a cube axis,

(2) The application of a field of 160 kG below the spin-flip temperature produces a "2-**Q** state," with the two remaining **Q**'s perpendicular to the applied field. The magnetic reflections in either the "single-Q" or "2-Q" states do not show any significant temperature hysteresis.

Both of the above effects were observed by neutron diffraction after the removal of the field.

We have observed the magnetic reflections about the (100) position in the presence of a magnetic field applied along the (100) direction. Fields up to 12.4 kG do not affect the intensity of the $(1-\epsilon, 0,0)$ or the $(1+\epsilon, 0,0)$ reflection, but the $(1,\epsilon,0)$ and $(1,0,\epsilon)$ reflections are increased in intensity. This result indicates a decrease in the volumes of domains which have their polarization parallel to the applied field. The percent increase in these reflections as a function of field is shown in Fig. 7. This field effect is entirely reversible for fields less than 12.4 kG.

These experiments could also be interpreted as a rotation of the polarization within a given domain away from a cubic axis as a continuous function of field.

The shape of the $(1,0,\pm\epsilon)$ reflections [observed together in this experiment] is shown in Fig. 8 in the presence of a 12.4-kG field, and in zero applied field. The shape of the two curves is identical. In addition the peak is not shifted in position. This indicates that the wave vector $\mathbf{Q}_3$ is not rotated away from the $\hat{x}_3$ axis. The sensitivity of this experiment to a rotation of $\mathbf{Q}_3$ away from the $\hat{x}_3$ axis is about 2 min of arc.

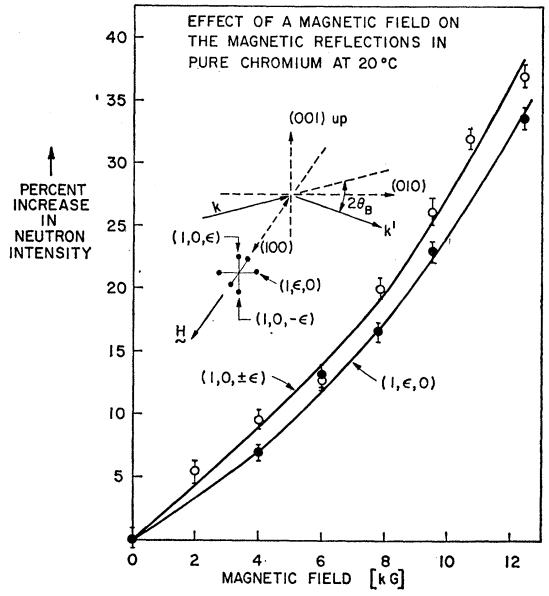

FIG. 7. These curves show the percent increase in the magnetic reflections $(1,0,\pm\epsilon)$ and $(1,\epsilon,0)$ as a function of field applied along the (100) direction.

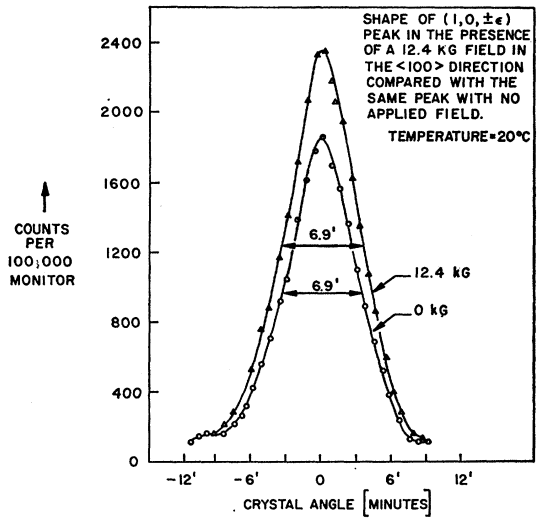

FIG. 8. Comparison of the shape of the reflections $(1,0,\epsilon)$ and $(1,0,-\epsilon)$ taken together in the presence of a 12.4-kG field and in the presence of zero field. Note that if $\mathbf{Q}_3$ had rotated away from a cube axis due to the application of the field, the curve would have either broadened, split, or shifted. None of these effects were observed.

These results certainly suggest that a continuation of this type of experiment to higher field, perhaps 40 kG, is desirable. At present, we do not have a magnet spectrometer which can reach these fields. At very large fields we might expect that the domains having their **Q** vectors perpendicular to the applied field will rotate to being parallel. At intermediate fields, say up to ~30 kG, we would expect the curves of Fig. 7 to saturate. Whether or not these curves saturate before **Q** starts to switch is not known. It would also be desirable to conduct high-field experiments at various temperatures, both below and above the spin flip.

IV. DISCUSSION

The de Haas–van Alphen data given by Graebner and Marcus[14] have resolved the question of whether the magnetic state of a given domain in chromium is "single-Q" or "multi-Q." Since no new de Haas–van Alphen periods appear when the crystal is transformed (by field cooling) from a "3-Q" state to a "single-Q" state, the Fermi surface is undoubtedly not changed. Consequently, the magnetic state of a given domain is one in which there is a single magnetization wave. This conclusion is fundamental in the interpretation of the domain structure made in this paper. This creates a paradox which remains unsolved in view of the fact that for a "single-Q" state to exist, the Fermi surface must be tetragonal, and this tetragonality should show up in the crystallographic structure. We have not been able to detect any differences in the three (1,0,0)-type

[14] J. Graebner and J. A. Marcus, J. Appl. Phys. 37, 1262 (1966).

x-ray reflections. The sensitivity of these x-ray experiments was 1 part in $\sim 2\times 10^4$.

It is clear from the neutron-diffraction data that the magnetization wave associated with a given $\mathbf{Q}$ vector is not helical. First of all, for a helical wave to exist above the spin-flip temperature would require that the average moment on a chromium atom must change by $\sqrt{2}$ at the spin flip in order to account for the fact that the average total intensity of the magnetic reflections around the three (100)-type positions does not change at this transition point.[15] In addition, the magnetic reflections $(1,0,\epsilon)$ and $(0,1,\epsilon)$ would be equal [when observed with the (001) axis vertical]. The ratio of these two reflections depends on the magnetic and thermal history of the sample, and under certain conditions the intensity of one of these has been observed to be close to zero. This fact also supports the model that the time-averaged spin direction is a cubic axis.

The antiphase model proposed originally for chromium by Corliss, Hastings, and Weiss[16] and reiterated by Bacon[6] is clearly not correct. Shirane and Takei[8] made a search for the third harmonic which this model predicts and were unable to see any trace of higher harmonics. The neutron diffraction results on all of the crystals we have examined confirm this conclusion.

There are a number of neutron diffraction experiments which remain to be done on pure chromium. The most readily accessible of these experiments are to extend the magnetic-field experiments to higher fields and to observe the changes in the structure as a function of pressure at low temperatures. The interpretation of the de Haas–van Alphen measurements on chromium may depend on these high-field neutron diffraction studies since the large fields used in the de Haas–van Alphen effect may, in fact, be changing the state of the sample. Critical scattering experiments on a crystal grown by strain and anneal have been performed by Møller *et al.*[17] We have pointed out in a previous paper[2] that it is difficult to distinguish between critical scattering and the Bragg scattering from domains which have decreased in size (yet are held antiferromagnetic by strain) causing a broadening of the coherent, magnetic Bragg reflections as the temperature is raised through the Néel point. In order to obtain meaningful critical scattering data, it is necessary to have a strain-free sample. The principal difficulty is one of intensity. The crystals which are grown from the vapor are probably the most strain-free samples available. However, these samples are generally less than about 100 mm^3 in size. There are a number of alternatives which may be pursued in solving this experimental difficulty. The one which we are now in the process of establishing involves the use of 10 detectors with small apertures placed on an arc, and centered on a vapor-grown crystal. This decreases the time necessary to obtain meaningful data by a factor of 10 and should permit this experiment to be done at a medium-flux reactor facility.

A. Model for the Magnetic-Field Effects in Chromium

The torque magnetometer measurements of Montalvo and Marcus[18] revealed the following magnetic field effects which are intimately connected with results of this paper:

1. When a chromium crystal was cooled through T_N in the presence of a large magnetic field directed along a cubic axis, the resulting torque curve showed twofold symmetry about an axis perpendicular to the field cooling direction.
2. If the crystal was cooled through T_N in zero applied field, the torque curve showed fourfold symmetry.
3. The magnitude of the torque in the first case was linear with the square of the measuring field; and in the second case was linear with the fourth power of the measuring field (for fields to 15 kG).
4. The twofold torque was about an order of magnitude larger than the fourfold torque. In both cases the torque increased with decreasing temperature.

In order to explain these results and the neutron diffraction data in this paper we make the following assumptions:

1. The energy necessary to move or create a "polarization wall" is small.
2. The potential barrier to rotation of the polarization direction from transverse to longitudinal is very large above T_{SF}. Thus, the spins are held in a transverse plane for each $\mathbf{Q}$ vector independent of applied field.
3. The anisotropy energy has fourfold symmetry about each $\mathbf{Q}$ vector with its minimums along the cubic axes perpendicular to $\mathbf{Q}$.

Consider now the effect of a magnetic field $\mathbf{H}_0$ applied in the (001) plane as shown in Fig. 9. φ is the angle between $\mathbf{H}_0$ and the [100] axis. The simplest form to choose for an anisotropy energy density having fourfold symmetry about $\mathbf{Q}_1$ is

$$E_{\text{anisotropy}} = K \sin^2 2\theta_1 \quad (\text{for } \mathbf{Q}_1), \tag{6}$$

where θ_1 is the angle between the polarization direction and [010]. The magnetic energy density created by applying the field H_0 will be

$$E_{\text{field}} = -\tfrac{1}{2}[\chi_\perp \sin^2\beta_{\mathbf{H}_0,\mathbf{p}_1} + \chi_{\parallel} \cos^2\beta_{\mathbf{H}_0,\mathbf{p}_1}]H_0^2 \quad (\text{for } \mathbf{Q}_1), \tag{7}$$

where $\beta_{\mathbf{H}_0,\mathbf{p}_1}$ is the angle between $\mathbf{H}_0$ and the polarization

[15] See the powder data of Ref. 7. We have found that the average moment does appear to increase by about 2% with increasing temperature at the spin flip. However, this result may be due entirely to small extinction effects.

[16] L. Corliss, J. Hastings, and R. J. Weiss, Phys. Rev. Letters **3**, 211 (1959).

[17] H. B. Møller, K. Blinowski, A. R. Mackintosh, and T. Brun, Solid State Commun. **2**, 109 (1964).

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

$\mathbf{p}_1$. $\chi_\perp$ and $\chi_\parallel$ are the susceptibilities for a field applied perpendicular and parallel to $\mathbf{p}_1$, respectively. Thus, for a given angle θ_1 of the polarization $\mathbf{p}_1$, we have, for the energy per unit volume,

$$E_{Q_1}=K\sin^2 2\theta_1+\tfrac{1}{2}\Delta\chi H_0^2\sin^2\varphi\cos^2\theta_1-\tfrac{1}{2}\chi_\perp H_0^2, \quad (8)$$

where $\Delta\chi=\chi_\perp-\chi_\parallel$.

A plot of this function versus θ_1 is shown in Fig. 10. We note there are two stable positions for $\mathbf{p}_1$, i.e., at 0° and 90°. The total energy associated with a domain oriented at θ_1 is $E_{Q_1}\delta V$, where δV is the volume of the domain. If this energy is of the order of kT, we would expect that domains that were originally oriented at $\theta_1=90°$ could be thermally excited to $\theta_1=0°$, or to any other angle for that matter. We note that the potential well at 90° becomes deeper as H_0 is increased (if $\Delta\chi>0$). Thus, one will expect the largest percentage of the domains to have their polarization near $\theta_1=90°$ for large fields. When this field is removed, the depth of the wells at $\theta_1=0°$ and $\theta_1=90°$ will be equal, and ultimately there will be an equal number of domains near $\theta_1=0°$ and $\theta_1=90°$. There will be a time constant associated with this equalization process. That is, after the magnetic field is released, the distribution of polarization domains will relax to the zero-field distribution. An externally applied stress will also perturb the distribution of polarization domains. Marcus and Arko[19] have shown the equivalence of a 32-kG field and an applied stress of a few kilograms per square millimeter. In order to explain the frequency dependence observed in the measurement of the mechanical properties of chromium (Young's modulus, magnetoacoustic damping), Street[20] points out that there must be a relaxation mechanism operating between T_{SF} and T_N. Below the spin-flip temperature T_{SF}, the degree of freedom associated with each polarization domain is lost since the polarization is then longitudinal.

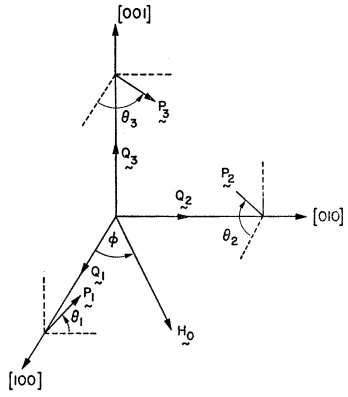

FIG. 9. Sketch showing the orientation of the three transverse polarizations $\mathbf{p}_1$, $\mathbf{p}_2$, and $\mathbf{p}_3$ relative to an applied field $\mathbf{H}_0$ in the (001) plane.

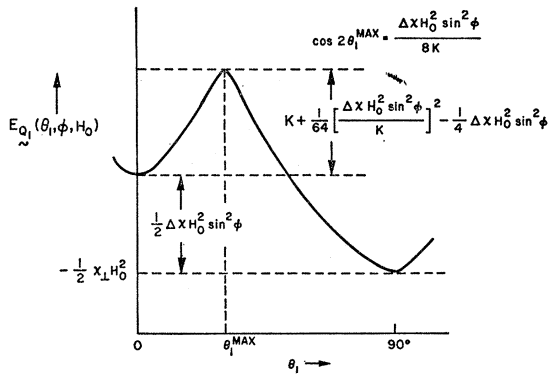

FIG. 10. Plot of the energy density associated with $\mathbf{Q}_1$ as a function of the orientation angle θ_1 of the transverse polarization $\mathbf{p}_1$.

If the applied field (or stress) oscillates in time rapidly, the thermal equilibrium distribution of polarization domains appropriate to each value of H_0 cannot be established. If the oscillations are extremely fast, the distribution of domains will not "see" the perturbation and will remain in a configuration appropriate to zero applied field (or stress). Any anomalous behavior in the mechanical properties will consequently disappear at high frequencies due to the inability of the system to follow the oscillating perturbations.

An alternative relaxation mechanism is one in which the strains relax by spin-density wave transitions,[21] for which there will also be a characteristic relaxation time. If these times were of the order of seconds, it would be possible to observe the relaxation process by neutron diffraction. However, from the frequency dependence of the mechanical properties of chromium, Street concluded that a characteristic time is less than 10^{-5} sec.[20] This conclusion is in agreement with our observation that the rotation of polarization domains is reversible when changes in the applied field are made on a time scale of the order of minutes.

The energy densities associated with $\mathbf{Q}_2$ and $\mathbf{Q}_3$ can be written down in a manner analogous to Eq. (8). The results are

$$E_{Q_2}=K\sin^2 2\theta_2+\tfrac{1}{2}\Delta\chi H_0^2\cos^2\varphi\cos^2\theta_2-\tfrac{1}{2}\chi_\perp H_0^2, \quad (9)$$

$$E_{Q_2}=K\sin^2 2\theta_3+\tfrac{1}{2}\Delta\chi H_0^2\cos^2(\theta_3-\varphi)-\tfrac{1}{2}\chi_\perp H_0^2. \quad (10)$$

Since we will be calculating statistical averages of angular-dependent functions, we can set the constant term $-\frac{1}{2}\chi_\perp H_0^2$ in (8), (9), and (10) equal to zero as a reference level of energy.

At thermal equilibrium the number of domains with $\mathbf{p}_1$ oriented in $d\theta_1$ at θ_1 will be

$$n_1(\theta_1)d\theta_1=c_1\exp[-E_{Q_1}(\theta_1)\delta V/kT]d\theta_1, \quad (11)$$

[19] J. A. Marcus and A. J. Arko, in *Proceedings of the Ninth International Conference on Low-Temperature Physics, Columbus, Ohio, 1964*, edited by J. G. Daunt, D. V. Edwards, F. J. Milford, and M. Yaqub (Plenum Press, Inc., New York, 1965), Summary CA5.

[20] B. C. Munday, A. R. Pepper, and R. Street, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (Institute of Physics and the Physical Society, London, 1965) pp. 201; R. Street, Phys. Rev. Letters **10**, 210 (1963); M. E. deMorton, *ibid.* **10**, 208 (1963).

[21] A. W. Overhauser, Phys. Rev. **128**, 1437 (1962).

where δV is an average domain size, c_1 is a constant determined from normalization

$$\int_0^{2\pi} n_1(\theta_1)d\theta_1 = V_{Q_1}/\delta V. \tag{12}$$

V_{Q_1} is the volume of the crystal occupied by domains having a wave vector $\mathbf{Q}_1$.

If we assume that $E_{Q_1}\delta V/kT$ is sufficiently small to expand the exponential, keeping only the first two terms, we find

$$c_1 = \frac{V_{Q_1}}{2\pi\delta V}\left[1-\frac{\delta VK}{2kT}-\frac{\delta V\Delta\chi H_0^2\sin^2\varphi}{4kT}\right]^{-1}. \tag{13}$$

B. Torque in a "Single-Q" State

We suppose now that the crystal is in a "single-Q" state with only $\mathbf{Q}_1$ represented. The energy associated with domains oriented in $d\theta_1$ at θ_1 is

$$dF_{\mathbf{Q}_1} = E_{Q_1}(\theta_1,\varphi)n_1(\theta_1,\varphi)\delta V d\theta_1. \tag{14}$$

Thus the energy of all of these domains is

$$F_{\mathbf{Q}_1}(\varphi) = \int_0^{2\pi} E_{Q_1}n_1\delta V d\theta_1, \tag{15}$$

and the torque created by the field is

$$\tau_{\mathbf{Q}_1} = -\frac{\partial F_{Q_1}}{\partial\varphi} = -\delta V\left[\int_0^{2\pi}\frac{\partial E_{Q_1}}{\partial\varphi}\,n_1 d\theta_1 + \int_0^{2\pi} E_{Q_1}\frac{\partial n_1}{\partial\varphi}d\theta_1\right]. \tag{16}$$

Calculation to first order in $(1/kT)$ gives

$$\tau_{\mathbf{Q}_1} = -\frac{\Delta\chi H_0^2 V_0}{4}\sin 2\varphi + \frac{V_0\delta V}{16}\frac{(\Delta\chi H_0^2)^2}{kT}\sin^2\varphi\sin 2\varphi, \tag{17}$$

where V_0 is the volume of the crystal. Thus for $\delta V \times \frac{1}{2}\Delta\chi H_0^2/kT$ small in comparison to 1, we note that the torque in a "single-Q" state has twofold symmetry, and that its magnitude is proportional to H_0^2.

C. Torque in a "Multiple-Q" State

If the crystal is cooled through the Néel point in zero applied field, all three $\mathbf{Q}$ vectors will be represented (nearly equally in a sample with randomly oriented microscopic strains). Performing the same operations as indicated by Eq. (16) for domains having wave vectors $\mathbf{Q}_2$ and $\mathbf{Q}_3$, we obtain the corresponding torques:

$$\tau_{\mathbf{Q}_2} = \frac{\Delta\chi H_0^2 V_{Q_2}}{4}\sin 2\varphi - \frac{V_{\mathbf{Q}_2}\delta V(\Delta\chi H_0^2)^2}{16kT}\cos^2\varphi\sin 2\varphi \tag{18}$$

and

$$\tau_{\mathbf{Q}_3} = 0. \tag{19}$$

Thus, if the volumes $V_{\mathbf{Q}_1}$ and $V_{\mathbf{Q}_2}$ are equal, namely,

$$V_{\mathbf{Q}_1} = V_{\mathbf{Q}_2} = \tfrac{1}{3}V_0, \tag{20}$$

then the torque in a "multi-Q" state of equal population can be seen to be

$$\tau_{\mathbf{Q}_1}+\tau_{\mathbf{Q}_2}+\tau_{\mathbf{Q}_3} = -\frac{V_0\delta V}{96}\frac{(\Delta\chi H_0^2)^2}{kT}\sin 4\varphi. \tag{21}$$

It is interesting to note that the magnitude of this torque is considerably less than for the "single-Q" state. It has fourfold symmetry, is linear in H_0^4, and is temperature-dependent.

Whether the truncation of the expansion of the temperature factor after the first two terms is satisfactory will depend on the size of the domains, δV; and will probably be justified for some crystals, but not for others. It appears to give satisfactory results for the crystal used in the torque measurements of Montalvo and Marcus. However, for our Cr-1 crystal, it appears that the domain volume is slightly too large for this approximation to be entirely valid.

D. Torque Below T_{SF}

We assume that the potential barrier to a rotation of the direction of polarization to transverse from longitudinal below the spin flip is very large. Thus, the energy density associated with each of the $\mathbf{Q}$ vectors is

$$\begin{aligned} E_{\mathbf{Q}_1} &= -\tfrac{1}{2}[\chi_\perp\sin^2\varphi+\chi_{\parallel}\cos^2\varphi]H_0^2, \\ E_{\mathbf{Q}_2} &= -\tfrac{1}{2}[\chi_\perp\cos^2\varphi+\chi_{\parallel}\sin^2\varphi]H_0^2, \\ E_{\mathbf{Q}_3} &= -\tfrac{1}{2}\chi_\perp H_0^2. \end{aligned} \tag{22}$$

Thus, the torque in a "single-Q" state (with only $\mathbf{Q}_1$ represented) is

$$\tau_{\mathbf{Q}_1} = +\tfrac{1}{2}\Delta\chi V_0 H_0^2\sin 2\varphi. \tag{23}$$

Comparing this with Eq. (17) indicates that the twofold torque should double in magnitude and reverse sign at the spin-flip temperature. The torque resulting from the field H_0 for a "multi-Q" state (of equal population) is identically zero below the spin-flip temperature. These results are in qualitative agreement with the experiments of Montalvo and Marcus; and where quantitative comparison is appropriate the agreement is also good.

E. Neutron-Diffraction Results

A neutron-diffraction experiment measures the average squared component of the magnetization which is perpendicular to the scattering vector. Thus, for the experiments described in Sec. III, in which the $(1,0,\pm\epsilon)$ reflections were observed, it is necessary to calculate the average $\langle[\mathbf{M}_q\cdot\hat{y}]^2\rangle_{\rm av}$, where $\hat{y}$ is a unit vector in the [010] direction, and $\mathbf{q}=(2\pi/a)(1,0,\pm\epsilon)$. Defining $p(\theta^3)$ as the probability for the polarization $\mathbf{p}_3$ to be in $d\theta_3$ at θ_3, we have for the neutron-diffraction intensity at $[1,0,\pm\epsilon]$

$$I(H_0)\propto\langle[\mathbf{M}_q\cdot\hat{y}]^2\rangle_{\rm av}=|\mathbf{M}_q|^2\int_0^{2\pi}\sin^2\theta_3 p(\theta_3)d\theta_3, \quad (24)$$

where

$$p(\theta_3)=\exp\left(-\frac{\delta V E_{Q_3}}{kT}\right)\Big/\int_0^{2\pi}\exp(-\delta V E_{Q_3}/kT)d\theta_3.$$

To first order in $1/kT$, Eq. (24) gives

$$I(H_0)\propto|\mathbf{M}_q|^2\left[\frac{1}{2}+\frac{1}{16}\frac{\Delta\chi H_0^2\delta V}{kT}\right]. \quad (25)$$

Thus, the percentage increase in the intensity of the $[1,0,\pm\epsilon]$ reflections as a function of field is

$$\frac{I(H_0)-I(0)}{I(0)}=\frac{1}{8}\frac{\Delta\chi H_0^2\delta V}{kT}. \quad (26)$$

For a field of 12.4 kG, this ratio is $\sim$0.35 at room temperature (20°C). The torque-magnetometer measurements of Montalvo and Marcus gave $\Delta\chi=0.2\times10^{-6}$ emu/g below the spin-flip temperature. (The measurements above $T_{\rm SF}$ are complicated by the rotation of the polarization as a function of applied field.) Using this value for $\Delta\chi$, one obtains $\delta V\sim4\times10^{15}$ Å^3, or that a characteristic domain dimension is $\sim1.6\times10^5$ Å. This number should be regarded as approximate in view of the fact that a value of $\Delta\chi$ at room temperature should be used, and that the ratio given in Eq. (24) is somewhat too large in order to justify retaining only the linear term in $1/kT$.

F. Field Cooling

We have shown in two previous papers[1,2] that applying a magnetic field greater than about 24 kG in the [010] direction during cooling through T_N produces a "single-**Q**" state with only $\mathbf{Q}_2$ represented. These results were confirmed in the neutron-diffraction experiments of Bastow and Street[9] and are inherent in the torque-magnetometer results of Montalvo and Marcus. These experiments show that the polarization has a strong preference to be perpendicular to an applied field. This indicates that $\chi_\perp>\chi_\parallel$. The preference for the spins to be perpendicular to the applied field was also observed in the experiment in which we applied a 160-kG field along $\mathbf{Q}_1$ below the spin-flip temperature, and only domains with wave vectors $\mathbf{Q}_2$ and $\mathbf{Q}_3$ remained. Apparently, the critical field in this case is near 110 kG.[22]

If the interaction of the spin system with a magnetic field is simply one in which the polarization direction prefers to be perpendicular to the field, the following question immediately arises:

Why is it that a state containing all three **Q** vectors with $\mathbf{p}_3\|[010]$, $\mathbf{p}_2\|[001]$, and $\mathbf{p}_1$ in the (100) plane does not result in a field cooling experiment when the cooling field is along the [100] axis?

We propose the following model to account for the fact that states with **Q** perpendicular to the applied field are suppressed even though their polarizations could be perpendicular to the field. This model is consistent with the explanations given above of the torque curves and the change of magnetic intensity in a magnetic field. We postulate that each "single-Q" region of the crystal will spontaneously break up into a series of domains with the polarization varying from domain to domain. (We might visualize these polarization domains as parallel plates perpendicular to **Q**.) The driving force for this is the increased entropy from the presence of the domains. Hence the energy per wall must be quite small. As the energy per wall should increase with decreasing wall spacing through what we will term a "wall-wall" interaction, there will be an equilibrium number of domains per unit volume. Thus the lowest energy state is presumed to be "single-Q" with many polarization walls. If a magnetic field is applied parallel to **Q**, the energy of all the domains will decrease according to $\frac{1}{2}\chi_\perp H_0^2$, but if the field is applied perpendicular to **Q**, the energy of domains with polarization not perpendicular to $\mathbf{H}_0$ will have less decrease in energy than those with polarization perpendicular to $\mathbf{H}_0$. If $\mathbf{H}_0$ is perpendicular to **Q**, the state of single polarization (perpendicular to H_0) is of lowest internal energy, but this state can be achieved only with the loss of the entropy gained from forming polarization domains.

A quite similar argument could be made with the strain field replacing the magnetic field. Thus in the absence of a magnetic field, the strain fields should determine **Q**. If the strain fields vary across the crystal, cooling in the absence of magnetic field should produce "multi-**Q**" crystals. Similarly in the presence of a magnetic field or a uniform strain field, one should get a "single-**Q**" crystal. (For strain fields the preference for a "single-**Q**" is only for tension, for compression there is an absence of that **Q** which is parallel to the compression direction.) The facts that one needs a certain threshold field to create a "single-**Q**" crystal, that this threshold field is different along the three cube

[22] B. R. Watts, Phys. Letters **10**, 275 (1964).

edges, and that it is quite different from crystal to crystal are all consistent with the need to overcome the effects of strain fields before the magnetic field is effective in determining which **Q** is preferred. In this model we have presumed that the energy to create walls between regions of different **Q** vectors is much larger than that for creation of polarization walls within "single-**Q**" regions. We note in this connection that in a field of 12 kG there is no difference in the volumes associated with each **Q** for a "multi-**Q**" crystal, and that applying and removing a 30-kG field produced no change in a "single-**Q**" crystal when the field was applied perpendicular to **Q**. With this model we would expect the crystals to be more likely "single-**Q**" the greater their freedom from inhomogeneous strain. This is in agreement with the findings of Graebner and Marcus who found that the vapor-grown crystals with the highest ratio of room temperature to residual resistivity were the most likely to be anisotropic when cooled in zero field.

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Paraelectric-Ferroelectric Phase Boundaries in Semiconducting Perovskite-Type Crystals

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The formation of first-order paraelectric-ferroelectric phase boundaries in semiconducting crystals of the ferroelectrics $KTa_{0.65}Nb_{0.35}O_3$ and $BaTiO_3$ has been studied. It is shown that in crystals having carrier concentrations greater than 10^{16} cm^{-3}, sharp first-order phase boundaries can form during the paraelectric-ferroelectric phase transformation, and that such a transformation results in the formation of reproducible single-domain crystals. The direction of the cubic-to-tetragonal phase boundary is found to differ from a {110} lattice plane by approximately 5°, i.e., the boundary-plane normal is 40° from the direction of the crystal *c* axis. This result is in excellent agreement with existing crystallographic theories. Data are also presented on the infrared photo-ionization absorption anisotropy and the electrical resistance anisotropy measured on a single-domain semiconducting crystal of $KTa_{0.65}Nb_{0.35}O_3$.

INTRODUCTION

It has been well established that an insulating ferroelectric crystal, when cooled through one of its transition temperatures, undergoes a metastable nucleation process that results in a variety of possible multiple-domain configurations which are generally nonreproducible. In semiconducting ferroelectric crystals, on the other hand, the situation should be quite different because the free charges present can compensate, or neutralize, the bound polarization charges inside the crystal thereby making possible the formation of reproducible single-domain crystals. We have observed, for example, that upon cooling a thin rectangular slab of the semiconducting ferroelectric $KTa_{0.65}Nb_{0.35}O_3$ (hereafter abbreviated KTN) through its cubic-tetragonal phase transition a sharply defined boundary forms dividing the crystal into a paraelectric (cubic) and a ferroelectric (tetragonal) phase. This first-order phase boundary or habit plane moves from one end of the crystal to the other during the phase transformation leaving behind a single domain ferroelectric crystal.

Such diffusionless phase boundaries in partially transformed single crystals are well known in metallurgy and have been studied extensively in a number of metal alloys, most notably the austenite-martensite transformation in steel.[1–4] Wechsler, Lieberman, and Read[2] (WRL) have shown theoretically that, when certain assumptions are made as to the detailed nature of the slip and/or twinning system, the direction of the habit-plane normal can be determined from a knowledge of the lattice parameters of the initial and final phases. Based largely on theoretical predictions, it was in fact suggested[4] some time ago that the WLR theory should be applicable to perovskite-type ferroelectric crystals. We believe that the results presented here give unambiguous experimental evidence for habit plane formation in these materials and that these results are quantitatively explainable in terms of the WLR crystallographic theory. It should be emphasized that such crystallographically determined boundaries are permitted only in semiconducting ferroelectrics where there is sufficient free charge available to provide a termination for the spontaneous polarization at the paraelectric-ferroelectric interface.

[1] See, for instance, J. W. Christian, *The Theory of Transformations in Metals and Alloys* (Pergamon Press, Inc., New York, 1965).
[2] M. S. Wechsler, D. S. Lieberman, and T. A. Read, Trans. AIME **197**, 1503 (1953).
[3] M. W. Burkart and T. A. Read, Trans. AIME **197**, 1516 (1953).
[4] D. S. Lieberman, M. S. Wechsler, and T. A. Read, J. Appl. Phys. **26**, 473 (1955).