ANOMALIES IN THE MAGNETIC STRUCTURE OF CHROMIUM

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The temperature dependence of the intensity of the magnetic satellites near points of the type (100) in the range 100-317°K and the effect of thermal hysteresis at room temperature for these reflections are measured by means of neutron diffraction. The magnetic form factor is assumed non-spherical. Two versions of the sinusoidal model of the magnetic structure of chromium are discussed.

THE first data on magnetic splitting of the peaks in neutron diffraction on chromium appeared in 1959 [1,2]. It follows from the work of Corliss et al.[2] that the intensity distributions around all points of type (100) (Fig. 1) are equivalent to each other. Our earlier paper [1] suggested the possibility of there being a magnetic structure in chromium, on the strength of differences between type (100) reflections which appear particularly prominently at low temperatures. Deviations from the equivalence were found also by Goman'kov et al.[3], who assumed in addition a superposition of a magnetic intensity on the nuclear peak (100). We have previously [1] reported a thermal hysteresis of the intensity of one of the magnetic reflections. On the other hand, Bacon did not find this phenomenon in his work on chromium [4].

These discrepancies induced us to carry out a new investigation to confirm the existence of "anomalies" in the magnetic scattering by chromium.

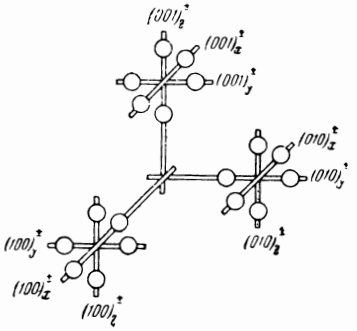

FIG. 1. Arrangement of magnetic reflections in reciprocal space.

EXPERIMENTAL

The measurements were done on a single crystal of chromium (made from chromium iodide) of 99.96% purity. The specimen had the

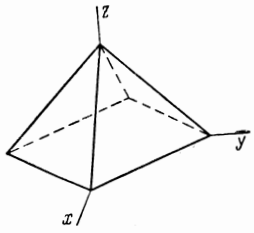

FIG. 2. Form of the main specimen.

form of a half-octahedron with the following dimensions: height 3 mm, side of base 4 mm. Figure 2 shows the chosen crystallographic directions in relation to the single crystal. The absence of a mosaic structure was checked optically with a double goniometer and with x-rays. The specimen was cooled by vapor from liquid nitrogen. The temperature was controlled to within ±2° by means of a copper-constantan thermocouple. The measurements were carried out with thermal neutrons of 1.25 Å wavelength monochromatized by reflection from a (111) plane of a single crystal of zinc. The reflections from the specimen had a half-width of 25′.

In order to determine the contribution of magnetic intensity to the superstructure points, the intensity of the (100), (010) and (001) peaks was measured in the temperature range 317-100°K. To eliminate accidental errors, each temperature curve was taken at least three times. Figure 3 shows averaged values of these measurements.

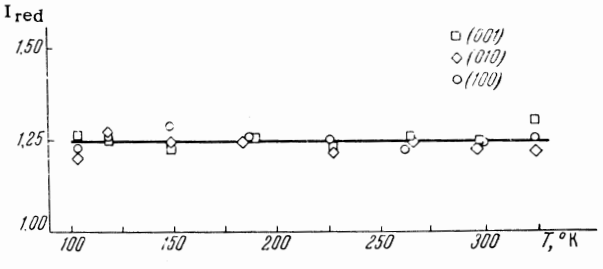

FIG. 3. Temperature dependence of the intensity of the (100) reflections. I_{red} is the reduced intensity.

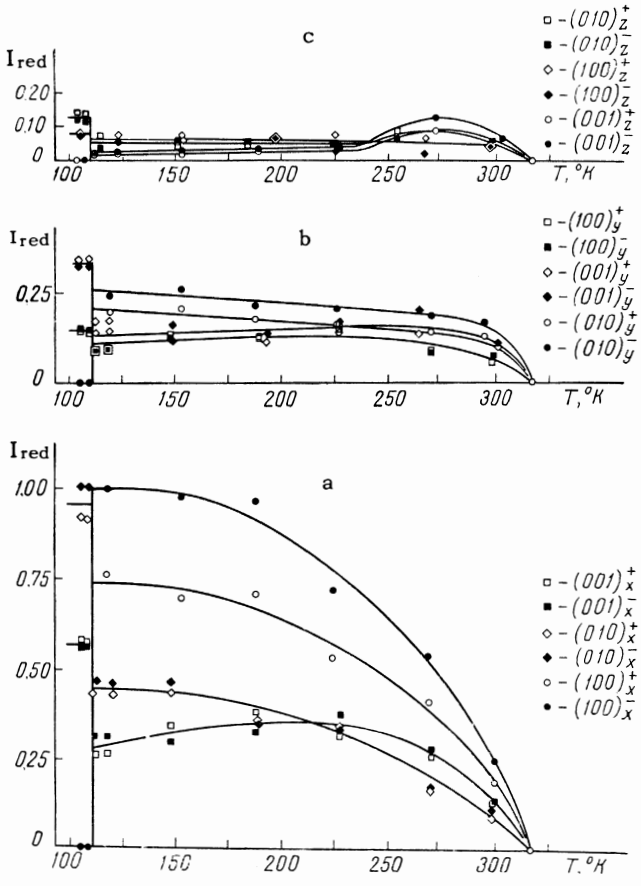

FIG. 4. Temperature dependence of the intensity of the magnetic reflections.

The experimental variation of intensity agrees satisfactorily with a Debye law. It follows that these peaks arise purely from the nuclear scattering of neutrons at half-wavelength. The good agreement of the intensities of the reflections (100), (010) and (001) at all temperatures shows that the cubic symmetry of the lattice of the nuclei is preserved. These fairly intense reflections are used in the further work as supplementary calibration to bring the magnetic reflections to a common scale. The differences in the intensity of the superlattice points did not exceed 10% after many changes in the position of the specimen.

Figure 1 shows the magnetic reflections studied and the notation used to identify them. The Miller indices are shown in brackets, the symbol x indicates the family of satellites whose splitting is parallel to the x axis, and the symbols + and − indicate the larger and smaller angle of the position of the crystal in the spectrometer. The notation is similar for satellites whose splitting is parallel to the y or z axis. Figure 4 shows the results of measurements of the temperature dependence of the intensity of the

Table I

T, °K	Intensity, %			T, °K	Intensity, %		
	x	y	z		x		z
293	50	33	17	173	71	22	7
283	60	27	13	143	73	21	6
233	67	25	8	113	73	21	6
203	71	22	7	103	71	21	8

satellites separately for the x, y and z families. The x family contains two "tetragonal" reflections $(100)_x^{\pm}$ and four "monoclinic" reflections $(010)_x^{\pm}$, $(001)_x^{\pm}$; similarly the y and z families contain "tetragonal" reflections $(010)_y^{\pm}$, $(001)_y^{\pm}$ and the "monoclinic" reflections $(100)_y^{\pm}$, $(001)_y^{\pm}$; $(100)_z^{\pm}$, $(010)_z^{\pm}$. The relative total intensities for each family [5] at various given temperatures are shown in Table I. It follows from the data in Table I and Fig. 4 that over the whole temperature range studied the x family has the highest intensities both of "tetragonal" and of "monoclinic" satellites. For the y family the intensities of the satellites of both types are smaller and the lowest intensities are those in the z family. It is clear that the non-uniformity in the magnetic intensity which exists already at room temperature increases strongly at lower temperatures. The ratio of the total "tetragonal" to "monoclinic" intensities in the x family is close to unity at all temperatures. For the y family this is true only at low temperatures. The curve for the temperature dependence of the total intensity of all magnetic satellites (Fig. 5) has the usual Brillouin form.

The curve for the temperature dependence of the intensity of individual peaks is noticeably different. If the temperature passes through the lower critical point the intensity of the "tetragonal" peaks disappears, but instead an equal amount of intensity is found in the growing "monoclinic" reflections, and the total intensity does not change. This is in agreement with the results of the work of Wilkinson et al. [6]

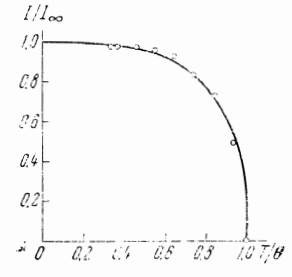

FIG. 5. Temperature dependence of the "total" magnetic intensity. The circles are experimental points, the curve is the theory (total angular momentum quantum number J = ½).

Table II

Indices	Intensity		Indices	Intensity	
	After annealing	After *l.t.* heat treatment		After annealing	After *l.t.* heat treatment
$(100)_x^{\pm}$	20.1	24.4	$(100)_z^{\pm}$	7.7	4.5
$(010)_x^{\pm}$	11.7	15.6	$(010)_y^{\pm}$	14.9	12.0
$(001)_x^{\pm}$	9.7	14.9	$(001)_y^{\pm}$	9.2	14.4
$(001)_z^{\pm}$	12.3	3.8	$(100)_y^{\pm}$	7.5	7.5
$(010)_z^{\pm}$	6.9	2.9			

The dimensions of our crystal satisfy the criterion of a "thin" specimen according to [7], and this was also confirmed by the equality of the intensity ratio of the nuclear peaks (100) and (200) for polycrystalline and single crystal chromium specimens. It was therefore possible to calculate from the total intensity the magnetic moment per atom of chromium without correction for secondary extinction. The magnetic moment was found to be $0.42 \pm 0.02\ \mu_B$, in good agreement with results which the authors have found in measurements on polycrystals and single crystals of chromium. The temperature variation of the magnetic structure parameter is shown in Fig. 6. The figure shows that this dependence is nonlinear. At 20°C, $\Lambda = 75$ Å, $\alpha = 1.8 \times 10^{-3}$/deg.

The occurrence of a thermal hysteresis, like the temperature dependence of the intensity of magnetic reflections, has been studied in this work for the same three families of magnetic satellites. The magnitude of the thermal hysteresis was measured for all peaks at room temperature. For this purpose the specimen was heated to 373°K, kept for five minutes and allowed to cool in air (~30 min) to room temperature. The neutron pattern from one pair of satellites was then recorded. The specimen was then cooled to 100°K in the vapour stream from liquid nitrogen, kept there for five minutes, and then warmed up in air to room temperature over about an hour. After this the pattern from the same pair of satellites was remeasured. The intensities of all magnetic reflections were measured in the same way. As a result of the low-temperature treatment the intensities of the magnetic peaks were different from those in the initial state, whereas their angular position did not change. The values of the modified intensities are shown in Table II and schematically represented in Fig. 7, where the broken circles indicate the intensities after the cold treatment. One sees that in the x family all magnetic intensities have increased, those in the z family have decreased, whereas in the y family the $(010)_y$ intensity has dropped, that of $(001)_y$ has increased, and the $(100)_y$ intensity is practically unchanged. The total intensity of all magnetic reflections is unchanged both after the first and after the second cycle with an accuracy of 1%, i.e., the intensity which is removed from some reflections reappears in others.

No special tests were made to ascertain how long the effect of the low temperature treatment persists; however, it was noticed that after a day the hysteresis effect was still present, whereas after a month it had completely disappeared.

For one pair of satellites for which the relative effect was greatest measurements were made on the temperature dependence of the hysteresis effect. The experiment was carried out in the same sequence as described above, except that the cooling went to various temperatures, and the exposure there was ten minutes. Figure 8 shows the change in the intensities of the $(001)_z$ reflections against the temperature to which the specimen was cooled. It is evident that the intensities of the reflections at room temperature vary linearly with the temperature of the treatment.

An attempt was made to discover the reason for the appearance of the non-uniform distribution

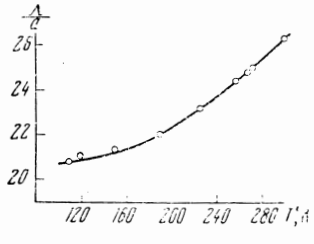

FIG. 6. Temperature dependence of the magnetic structure parameter Λ. a is the lattice spacing

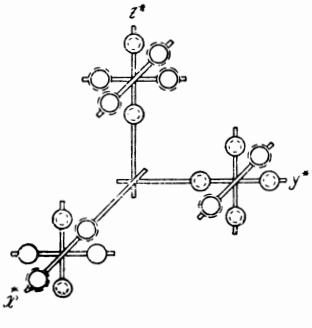

FIG. 7. Schematic diagram of the effect of the thermal hysteresis of the intensities of magnetic reflections.

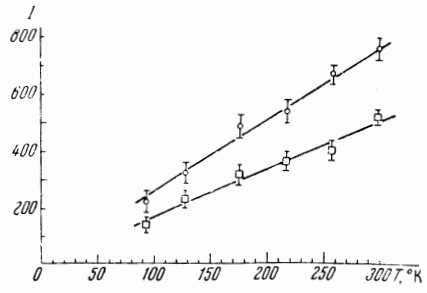

FIG. 8. Variation of the intensity of the reflections $(001)_x \pm$ at room temperature. The temperature to which the specimen was cooled is plotted horizontally.

of magnetic intensities over the directions in the single crystal. For this purpose four samples of chromium made from iodide were investigated: three crystals had a form similar to that shown in Fig. 2, two of them being free of mosaic structure whereas the third had a number of clearly visible regions; the fourth was different in that the cleavage was parallel to one face of the octahedron as shown in Figure 9. The "tetragonal" neutron reflections from the specimens described, which were taken for three directions, showed that all $(001)_z$ peaks had the lowest intensity compared to that of the two other directions. It may therefore be assumed that the pronounced nonequivalence in the intensity distribution from our specimens depends not on the form of the specimen but on some peculiarity of the real structure connected with the direction of growth of the crystal. The presence of mosaic structure in one of our specimens did not cause any particular changes in the intensity distribution.

DISCUSSION OF RESULTS

According to present diffraction theory splitting of the magnetic reflections into pairs of satellites will occur when the spin density in the crystal is subject to some modulation besides that due to the atomic structure. The most consistent model of the antiferromagnetic structure of chromium appears to be that involving a sinusoidal modulation.

There exist two versions of this model: the "three-domain" and the "one-domain" model. The three-domain version [5] assumes the existence of three kinds of domains each of which has a superstructure with its own wave vector $\mathbf{k}_\nu$, its own spin direction $\mathbf{S}_\nu$, and, as one can conclude from our experiment, its own substantially anisotropic magnetic form factor $f_\nu(\mathbf{s})$ ($\nu = x, y, z$). The one-domain version assumes the existence of domains of only one type which contain within themselves all three superstructures with the

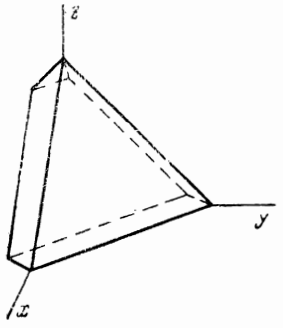

FIG. 9. Form of specimen.

parameters $\mathbf{k}_\nu$, $\mathbf{S}_\nu$, and f_ν. In this case $\mathbf{S}_\nu$ represents a spin component, and the different $f_\nu(\mathbf{s})$ mean that the anisotropy of the spin density cloud representing each component has a different orientation.

In the three-domain version the spin directions in the domains are fixed, but this will obviously not be the case in the one-domain model.

We shall discuss the experimental results in terms of the one-domain version, and then give an interpretation for the three-domain version.

The three magnetic superstructures of chromium correspond to three families of magnetic intensities I_ν. The wave vectors $\mathbf{k}_\nu$ which determine the positions of the satellites relative to the points of the reciprocal lattice, remain at all temperatures in directions parallel to the cubic axes of the lattice and equal in magnitude: $|\mathbf{k}_\nu| = 1/\Lambda$.

It is not surprising that the determination of the magnetic moment per chromium atom in the specimens under investigation leads to an answer compatible with that obtained from experiments on powder, since the unsplit powder lines arise from a natural addition of the intensities of the satellite peaks similar to the one we have carried out. However, if one takes into account the fact that in the sinusoidal model the splitting in two of the peaks reduces their intensity to a quarter, the value of the spin amplitude has to be taken larger by a factor $\sqrt{2}$ i.e., 0.59 μ_B. The total intensity for each family should, strictly speaking, depend on the direction of the spin components (because of the anisotropy of the magnetic form factor). However, Fig. 4 suggests that this variation lies within the limits of error of our experiment. One can therefore draw the following two conclusions from the data in Table I. Firstly, the spin components have substantially different values $|S_x| > |S_y| > |S_z|$. Secondly, as the temperature is lowered the ratios between these quantities change, i.e., $|S_x| = \beta_1(T)|S_y| = \beta_2(T)|S_z|$. The last fact demonstrates that a change in temperature causes a redistribution of the spin density

between its three regions.

From the shape of the "anomalous" curves (Fig. 4) one can deduce that the directions of the spin components also change with temperature. The component S_z forms at room temperature a fairly large angle with the wave vector k_z. At low temperatures (110-225°K) this angle becomes small. The component S_y turns with falling temperature from a direction near the space diagonal of the cube to a direction approximately normal to k_y. The component S_x forms at all temperatures an angle with k_x which is nearly a right angle, and the only appreciable change in its direction is in the plane at right angles to the wave vector. This qualitative picture of the directions of S_ν is correct provided the magnetic form factors do not vary appreciably with temperature.

At 110°K there is a change in the symmetry of the magnetic structure of chromium. Below 110°K all spin components are parallel to their wave vectors, and for all the measured reflections $q^2 = 1$; one can therefore evaluate the anisotropy of the magnetic form factor from the ratios of the intensities of the "monoclinic" peaks of one family. We find

$$|f_x(010)|^2 / |f_x(001)|^2 = 1.68,$$

$$|f_y(001)|^2 / |f_y(100)|^2 = 2.26,$$

$$|f_z(010)|^2 / |f_z(100)|^2 = 1.54.$$

From our experiments one cannot determine the magnetic form factors for temperatures above 110°K uniquely. For this one would have to have a picture of the distribution of magnetic intensity over a large region of reciprocal space. However, one can assume that the anisotropy of the magnetic form factor along the third direction is equal in magnitude to that already found for each of the families i.e., that $|f_x(100)|^2/|f_x(001)|^2 = 1.68$, etc. It is then easy to show that the change in the total intensity caused by the change in the direction of the spin components at 110°K will be comparable to the experimental error.

The measurements on the thermal hysteresis confirm and supplement the above conclusions about the spins. No thermal hysteresis for the total intensity is observed. Any inertia in the temperature dependence of the magnitude of the mean spin must therefore have a relaxation time below 10^3 sec. A temperature dependence of the distribution of spin density and a temperature dependence of the directions of the spin components therefore appear to be necessary conditions for the observed thermal hysteresis of the intensities of the individual peaks. One sees from Table II and Fig. 7 that the first of these is the dominant effect in the x and z families, and the second in the y family. The hysteresis demonstrates a definite inertia of these temperature variations with a relaxation time which can be estimated at 10^5-10^6 sec. The discussion in terms of the three-domain version of the model has the following features. In this version obviously $|S_x| = |S_y| = |S_z|$, so that we are dealing with the values of the amplitude not of the spin component but of the total spin in corresponding domains. One can therefore explain the differences between the I_ν by an unequal distribution of the volume of the specimen over the domains of different kinds, and in place of the temperature dependence of the distribution of spin density we may now talk of the temperature dependence of the division of the volume of the specimen; in place of the temperature dependence of the directions of spin components we now speak of the temperature dependence of the spin directions in the domains.

In support of each of these versions of the model we can give only very general arguments, which do not make it possible to give preference to either. Thus the redistribution of spin density with temperature seems a "simpler" process than the redistribution of the volume between the domains. On the other hand the thermal hysteresis effect which reflects an inertia of this process with a macroscopic relaxation time is a more familiar idea just in the case of changes in the macroscopic volume distribution.

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