Absolute X-Ray Measurement of the Atomic Scattering Factor of Chromium

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(Received 29 November 1971)

Absolute measurements were made to determine the atomic scattering factor of chromium by x-ray diffraction. This study was made at room temperature, using an imperfect single crystal in transmission and applying a measured secondary-extinction correction to the integrated intensities obtained with monochromatic MoKα radiation. The measurements were placed on an absolute scale using a value of the Debye temperature of 525 °K and a measured mass-absorption coefficient of 30.15 cm^2/g. As in previous measurements on nickel, the apparent scattering factors of the (110) and (200) reflections were found to depend linearly on the reciprocal of the reflection half-width, thus indicating the presence of primary extinction. The true atomic scattering factors for the (110) and (200) reflections, determined from an extrapolation to zero reciprocal half-width, were found to be considerably lower than the theoretical values obtained from free-atom Hartree-Fock calculations. From the paired reflections (330)-(411) and (600)-(442) the t_{2g} population of 3d electrons was found to be about 72%, thus indicating a marked departure from spherical symmetry.

INTRODUCTION

This paper is the second of a series concerned with measuring the atomic scattering factor of metals by x-ray diffraction.[1] As no accurate theoretical scattering factors are currently available for solids, experimental results are usually compared with free-atom Hartree-Fock calculations. Since these are believed accurate to approximately 1%, solid-state effects can be observed, if experiments are performed with comparable accuracy. In fact, most of the experimental values which have been reported for metals range from agreement with to about 5% less than free-atom theory. Chromium was chosen because we thought that a measurement on a metal with a crystal symmetry other than nickel and aluminum, which have already been investigated with the same technique,[1,2] could give some information on the role played by symmetry on charge distribution. In addition, the scattering factor of chromium has already been measured by Cooper[3,4] on a powder sample, up to the (521) reflection. His results show, for all the reflections investigated, that the measured scattering factor is about 5% lower than the free-atom theory. Because of the difficulties in obtaining perfect chromium single crystals we have chosen to carry out this experiment on a thin imperfect single crystal, as in our first paper. Therefore, our experiment will also be of interest in assessing the relative merits of the two techniques.

The experimental technique has been discussed elsewhere.[1,2,5] It is a method which enables one to obtain scattering-factor values free from secondary extinction, and to assess the amount of primary extinction, if present. In essence one measures integrated intensities in transmission from a very thin crystal using a narrow beam whose divergence is the order of a few minutes of arc. By simultaneously measuring the transmitted and diffracted power as the crystal is rocked through the reflection, it is possible to have a point-by-point correction for secondary extinction. To assess the amount of primary extinction, the squares of the scattering-factor values, obtained at different spots on the crystal surface, are examined as a function of the reciprocal half-width squared. From an extrapolation to infinite half-width a value of the scattering factor free from primary extinction can be obtained. Although this procedure cannot be rigorously justified, in the case of nickel, where this method has already been applied, the extrapolated values did not depend on the wavelength used. Moreover, a linear dependence of the square of the scattering factor on the square of the ratio of crystal thickness to reflection half-width has been actually observed for primary extinction up to 6%, showing that this procedure is correct, at least within these limits.

EXPERIMENT

The chromium single crystal was kindly supplied by AMMRC, Watertown, Massachusetts. It was obtained from 99.9$^+$% chromium, free from any high absorbing impurity. The crystal was grown from the melt, then spark planed and finally ground by hand to a thickness of approximately 50 μ through a series of abrasives. It was then given a light etch. The crystal was examined by a series of transmission Laue photographs taken over several locations on the crystal surface. The measurements were carried out using MoKα radiation monochromated by a singly bent LiF crystal. The

x-ray tube was operated between 40 and 44 kV to reduce the amount of second-order contamination. The amount of $\frac{1}{2}\lambda$ component actually present in the diffracted beam (approximately 0.1%) was completely eliminated by the use of pulse-height discrimination. The incident beam consisted of α_1 and α_2 wavelengths in the ratio of about 2:1. The reflections (110), (200), (211), and (220) were measured with an incident beam power of about 5000 counts/sec and a total circuitry dead time of 2 μsec. By the use of three pinholes the incident beam divergence was collimated to 3 minutes of arc, a factor of 3 less than the smallest half-width observed (this ratio, however, was higher than 5 in most cases), with a cross section of approximately 10^{-1} mm^2 at the surface of the crystal. For the high-angle reflections stronger beams were used to achieve an acceptable statistical accuracy. The single-crystal miscut was less than 1°, so that its effects could be eliminated by averaging two measurements performed on the same spot with the crystal rotated by 180°. The absorption factor was measured on the single crystal itself, determining the ratio of the transmitted to the incident beam at about 600 different locations on its surface. The value of the mass absorption coefficient obtained from two independent measurements was found to be $\mu/\rho = 30.15 \pm 0.3$ cm^2/g. All the data were corrected for thermal-diffuse scattering (TDS) using the Nilsson[6] correction as revised by Walker and Chipman.[7] For the paired reflections, a check on the possible anisotropy in the TDS factor was performed by means of the computer program developed by Walker and Chipman.[8] The difference on the scattering factors so computed amounted, for both pairs, to less than 0.1%. No attempt was made to measure the Debye temperature of the crystal from a high-angle reflection, as no reflection was certain to have a value of the scattering factor coincident with Hartree-Fock theory. For comparison purposes, at first, the same value used by Cooper,[4] namely 485 °K, was used. The scattering factors have been put on an absolute scale assuming $\Theta = 525$ °K. According to Wilson *et al.*'s experimental results[9] in fact, the room-temperature value of the Debye temperature for chromium falls between 525 and 565 °K. Since, however, the curve of Θ versus temperature calculated by Feldman[10] agrees with the above-mentioned results if Θ is taken to be 525 °K at room temperature, this latter value has been chosen.

As a check of the reproducibility of the high-angle results the (600) reflection was also measured in reflection from a thick single crystal of chromium. The value of the scattering factor so obtained differed from the one obtained in transmission by only 0.8%. This gives a good indication of the statistical uncertainties of the present results.

The comparison between the scattering factors calculated for $\Theta = 485$ and 525 °K, moreover, gives an indication of the sensitivity of our values to this parameter. A further source of error arises from the polarization factor, as no information was available concerning the state of perfection of our monochromator. Jennings[11] has shown that the polarization factor can be not only removed from the value expected on the basis of an ideally mosaic monochromator, but can not even lie between this value and that expected on the basis of an ideally perfect monochromator. It was also shown, however, that in the actual cases the polarization factor can exceed the perfect-monochromator value only very slightly.

For our measurements the difference in polarization factor between the ideally perfect and the ideally imperfect case is about 1% for the (220) reflection. As such, we have chosen to use for our calculations the average of the two values. Because of the above-mentioned uncertainties only the first four reflections have been put on an absolute scale and we estimate for them that the total error amounts to about 1.3%.

RESULTS

The measured values of $(f + \Delta f')^2 + (\Delta f'')^2$ for the first three reflections of chromium are shown in Figs. 1–3.

The secondary-extinction correction for these values ranges from a minimum of 0.7% to a maximum of 11.2% (see Table I). As discussed in the nickel paper,[1] the extrapolation of $(f + \Delta f')^2 + (\Delta f'')^2$ to infinite half-width gives a value free from primary extinction, regardless of the wavelength used, if the observed values depend linearly on T^2/Δ^2. Listed in Table II are the measured atomic scattering factors, with their errors, for both $\Theta = 485$ and 525 °K. The dispersion corrections used to obtain f are those of Cromer[12]. Also listed are the scattering factors measured by Cooper and the theoretical scattering factors for chromium in the $3d^5 4s$ configuration, calculated by Freeman and Watson.[13] As mentioned, we have reported only the values obtained from the first four reflections,

TABLE I. TDS correction and the range of secondary extinction measured for the chromium crystal with molybdenum radiation.

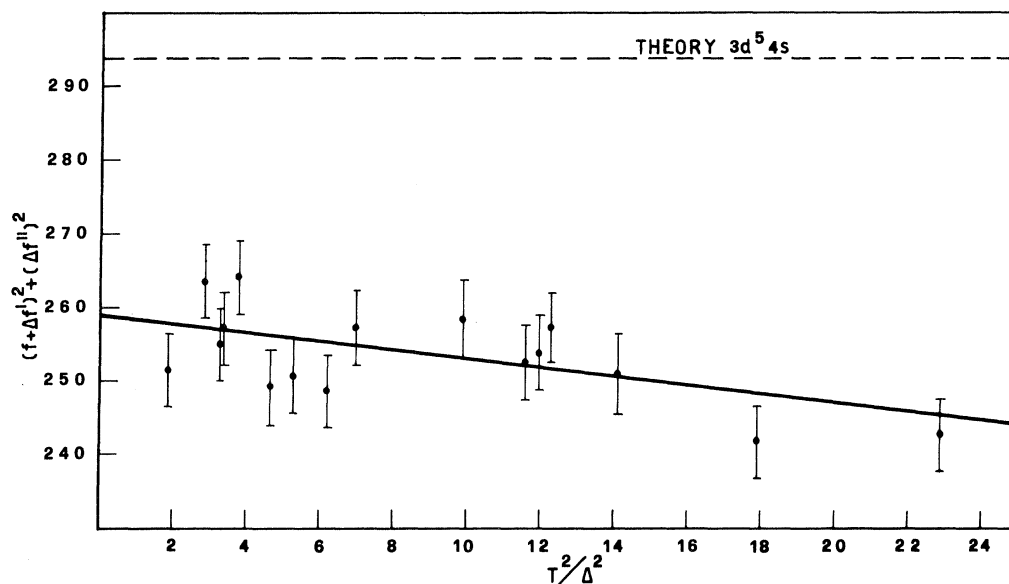| *hkl*	% TDS	% secondary extinction
(110)	0.18–0.26	2.9–11.2
(200)	0.39–0.54	2.9– 5.5
(211)	0.70–0.90	1.1– 3.5
(220)	1.02–1.30	0.7– 1.6

FIG. 1. Atomic scattering factors measured from the (110) reflection of chromium with $MoK\alpha$ radiation are shown as function of T^2/Δ^2. The solid line is the best least-squares straight-line fit for all values. All values shown have been corrected for secondary extinction.

as these are the only ones for which results can be obtained sufficiently accurate to allow their independent comparison with Hartree-Fock theory. The errors listed in Table II up to the (220) reflection are the square root of the sum of the squares of the errors arising from all sources of uncertainty.

It is readily seen that, if Θ is taken as 485 °K so that a comparison with Cooper's data can be made, the (110) and (200) scattering factors are practically the same in both experiments. For the other reflections, however, Cooper observed a larger difference from theory than we do. We conclude therefore, that in the case of chromium, at low scattering angles, differences of 4–5% between Hartree-Fock theory and experiment exist, regardless of the x-ray technique used. In connection with this we may remark that the scattering factors of the (110) and (200) reflections are practically independent of Θ. If 525 °K is assumed as a more plausible value of Θ, the difference between experiment and theory tends to increase, in particular at large $(\sin\vartheta)/\lambda$.
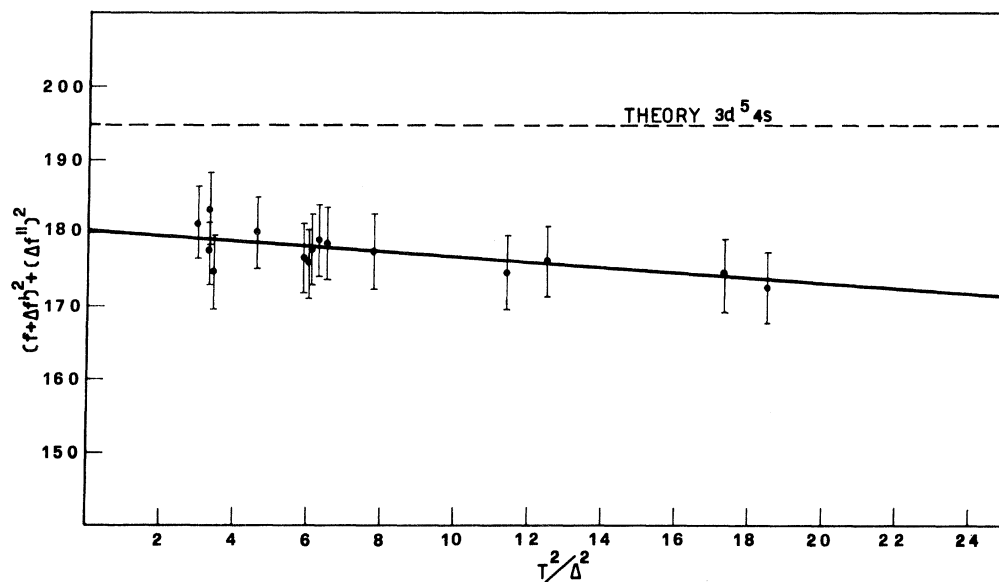

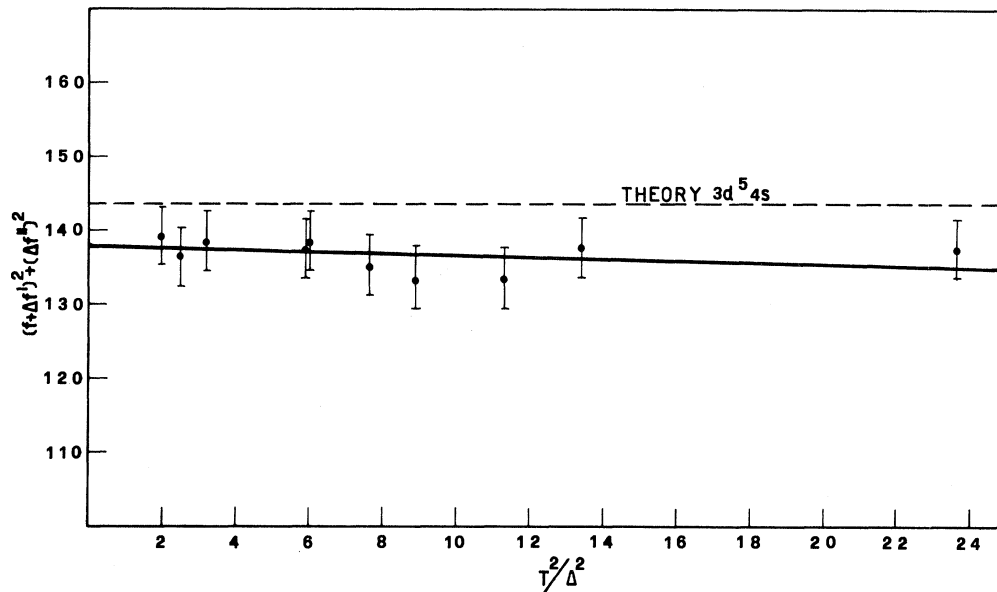FIG. 2. Same as in Fig. 1 for the (200) reflection.

FIG. 3. Same as in Fig. 1 for the (211) reflection.

It is interesting to notice that the difference between the free-atom scattering factors and the crystal ones is, to a good approximation, proportional to the value of the $3d$ scattering function in the free atom. This seems to indicate that the difference between experiment and theory in chromium can be entirely ascribed to an appreciable delocalization of some of the $3d$ electrons.

From the paired reflections (330)–(411) and (442)–(600) the percentages of $3d$ electrons having t_{2g} and e_g symmetry can be calculated, as discussed by Weiss.[14] These percentages only depend on J_4, that is, the integral of the product of the radial charge density and the fourth-order spherical Bessel function. As this integral, for the ground state of chromium, is not tabulated in the literature, we have used the values of J_4 calculated by Watson and Freeman[15] for the neutral $3d^6$ configuration and for the doubly ionized $3d^4$ state. This is because the

ground-state form factor of chromium is obtained from the singly ionized $3d^5$ state with the simple addition of the $4s$ scattering function. The results obtained for both sets of paired reflections are summarized in Table III. Depending on the choice of J_4 one obtains 76 and 72% t_{2g} for the (330)–(411) pair and 72 and 69% t_{2g} for the (442)–(600) pair. From these figures it is evident that chromium, as one would expect, tends to point its outer charge toward the nearest neighbors.

In summary it is possible to state that in chromium two solid-state effects are observed by x-ray diffraction: (i) The charge distribution is expanded with respect to free-atom calculations. This is similar to what has been found for all metals investigated to date (Al, Fe, Ni, Cu) with the only exception of Mg. In addition, this expansion seems to be entirely attributable to the $3d$ electrons. (ii) The $3d$ electrons, in the atomic-orbital picture,

TABLE II. Atomic scattering factors of chromium. The values quoted here are those calculated in Ref. 14. The relativistic values calculated by Doyle and Turner [P. A. Doyle and P. S. Turner, Acta Cryst. A24, 390 (1968)] have not been reported since, in the range here considered, they differ from the nonrelativistic ones by less than 0.5%. The experimental and calculated parameters involved in evaluating the measured x-ray intensities are $\lambda = 0.71069$ Å, $\mu = 216.9$ cm^{-1}, $a_0 = 2.8846$ Å, $\Delta f' = 0.34$, $\Delta f'' = 0.69$.

hkl	f_{theor}	f_{485}	f_{Cooper}	f_{525}	$\dfrac{f_{theor}}{f_{485}}$	$\dfrac{f_{theor}}{f_{Cooper}}$	$\dfrac{f_{theor}}{f_{525}}$
(110)	16.78	15.78 ± 0.20	15.93	15.74 ± 0.20	1.063	1.053	1.066
(200)	13.62	13.13 ± 0.17	13.11	13.06 ± 0.17	1.037	1.039	1.043
(211)	11.63	11.47 ± 0.15	11.12	11.37 ± 0.15	1.014	1.046	1.023
(220)	10.30	10.20 ± 0.14	9.84	10.10 ± 0.14	1.010	1.047	1.020

TABLE III. Percentages of $3d$ electrons having t_{2g} or e_g symmetry.

$f(330)/f(411) = 1.013 \pm 0.007$		
$J_4\|3d^{4++}$	$t_{2g} = 76\%$	$e_g = 24\%$
$J_4\,3d^6$	$t_{2g} = 72\%$	$e_g = 28\%$
$f(442)/f(600) = 1.014 \pm 0.007$		
$J_4\,3d^{4++}$	$t_{2g} = 72\%$	$e_g = 28\%$
$J_4\,3d^6$	$t_{2g} = 69\%$	$e_g = 31\%$

are approximately 72% in the t_{2g} sublevels and 28% in the e_g sublevels. This is in agreement with the measured population in the bcc metals iron[16] and vanadium,[17] and in contrast with nickel where, as one would expect, no marked asphericity effects are present.

ACKNOWLEDGMENTS

We are greatly indebted to J. J. De Marco for supplying the chromium crystal and for his help at all stages of the present research. We also want to thank Dr. C. B. Walker for kindly computing some TDS corrections, Dr. C. R. Natoli for many helpful discussions, and G. Menichelli for helping to collect the data.

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Theorem on the Magnetoconductivity of Metals

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(Received 3 December 1971)

Under rather general assumptions it can be proved that the conductivity of a metal is monotonically nonincreasing with magnetic field. In the proof given it is assumed that the electron motion can be described by a fermion Boltzmann equation with arbitrary multiple band structure and an arbitrary law of scattering. However, the magnetic field is to enter only through the Lorentz force term. Exceptions to the theorem are known; they arise probably because the magnetic field influences the scattering process.

A remark by Pippard[1] that the magnetoresistance can be proved positive under very general assumptions has led the author to investigate this question. The result of this investigation is the following much stronger theorem:

If the magnetic field acts on electrons in a band or band system only through its contribution to the Lorentz force, and if the behavior of the electrons is adequately described by a Boltzmann equation, then the electrical conductivity of a metal is a monotonically nonincreasing function of the magnitude of H. Conductivity is here defined as the number with which E^2 is to be multiplied to get the power dissipation per unit volume. The statement is restricted to the Ohmic range.

We shall outline the proof for a single band and indicate at the end its generalization to band systems. We take the behavior of the electrons to be controlled by an equation of the following form:

$$\frac{\partial f(\vec{k})}{\partial t} + \frac{e}{\hbar}\left(\vec{E} + \frac{1}{\hbar c}\frac{\partial W(\vec{k})}{\partial \vec{k}} \times \vec{H}\right) \cdot \frac{\partial f(\vec{k})}{\partial \vec{k}}$$