

Absolute measurement of the x-ray scattering factor of $\text{Co}_{0.91}\text{Fe}_{0.09}$

M. Diana and G. Mazzone

Laboratorio Caratterizzazione Materiali, Centro Studi Nucleari della Casaccia, 00100, Roma, Italy

(Received 1 May 1978)

Absolute measurements have been performed to determine the x-ray scattering factor of $\text{Co}_{0.91}\text{Fe}_{0.09}$. This study has been made using two imperfect single crystals in symmetrical transmission, and applying a measured secondary extinction correction to the integrated intensities obtained with Ag K α radiation. A measurement of the incident-beam intensity placed the results on an absolute scale. The experimental values of the scattering factors have been found to depend systematically on the reflection half-width, thus indicating the presence of primary extinction. The scattering factors for the (110) and (200) reflections, determined from an extrapolation to infinite half-width, have been found to be about 2% lower than the corresponding theoretical free-atom values. The measured asphericity of the total d charge ($\%t_{2g} = 61.5$) agrees with that calculated from a polarized-neutron measurement of the magnetic form factor of the same alloy.

INTRODUCTION

Accurate experimental values of the x-ray scattering factor of transitional metals make it possible to perform a significant check on the validity of band-calculated wave functions. Although contrasting results have often been obtained both from experiments and band calculations, in all cases the agreement of experiments with such calculations has been better than with free-atom theory. It is therefore presumable that a sustained experimental and theoretical effort will eventually lead to a better understanding of the methodology necessary in this field to obtain reliable physical information.

In a recent article Suortti and Jennings¹ have described in great detail, for a powdered sample, the correct procedure to separate the Bragg component from the total scattering and to relate the integrated intensity to the structure factor. Although a similar discussion for single-crystal experiments is entirely beyond the scope of this paper, it must be remarked that for a carefully prepared single crystal of a transitional metal, the peak-to-background ratio is sufficiently high (up to 10^3) to make the total background correction very small (2%–3%) with respect to the integrated intensity, even if the ω scan has to be made rather extended in order to accept the tails of the diffraction peak. In some cases, in fact, it has been found that such tails arise from the mechanical treatments necessary to increase the mosaic spread of the sample. If these conditions are met, the uncertainty on the background correction is, therefore, of the probable order of 1% of the integrated intensity. Concerning the conversion of integrated intensities to structure-factor values, apart from the knowledge of some physical properties of the solid, essentially one needs to know

the amount of extinction affecting the portion of sample under examination.

While an experimental procedure to correct for secondary extinction has been described and can be routinely applied,² if one wants to perform a correction for primary extinction, it is easy to show (following the treatment of Zachariasen³) that, in the symmetrical Laue case, even for the simple case of a mosaic crystal consisting of platelets of different thickness [assuming the angular distribution of mosaic blocks $W(\delta)$ to be independent of the thickness distribution $U(t)$], one needs to know the first and third moment of the thickness distribution. As this information is obviously not available, the correction for primary extinction can only be approximately performed, and, in our opinion, represents the main source of uncertainty in obtaining structure factors from single-crystal diffraction experiments. The procedure adopted by us has been described in previous papers,^{4,5} but it may be criticized on the grounds that, first, it is impossible to define the "correct" extrapolation procedure, and second, residual primary extinction may be present even for "infinite" half-width (physically this situation would correspond to a powdered sample). In the actual cases, the presumption that residual primary extinction is at most of the order of other experimental errors is justified by the use of different radiations and/or different crystals, since in both cases the extrapolation to infinite half-width should give different values for the structure factor, if still affected by primary extinction. Similarly, if the same structure factors are obtained from experiments performed on single crystals and powdered samples, one may reasonably conclude that the respective corrections, of a different nature and therefore physically independent in the two cases, have been correctly applied. Much clearer is the situation

for what concerns charge-density asphericity. Although such information can be obtained in principle also from a powder experiment, the measurement from a single crystal of the ratio of the structure factors of one or more reflection pairs is an experimental datum that, as extensively discussed,⁶ is practically free from any systematic error. In conclusion, it seems possible to state that the measured scattering factors, in addition to the statistical uncertainty arising from the imperfect knowledge of a number of parameters and corrections [density, mass absorption coefficient, Debye temperature, dispersion coefficients, polarization ratio, and thermal diffuse scattering (TDS)] suffer from some systematic errors (extinction, polycrystalline layer, amorphous scattering from grain boundaries) that all tend to decrease the measured integrated intensity. On the other hand, with suitable preparation of the sample, single-crystal measurements are not affected by most of the problems related to sample characterization typical of powdered specimens, and are scarcely sensitive to background choice.

As part of our program to measure the scattering factor of transitional metals, we have decided to study the alloy $\text{Co}_{0.91}\text{Fe}_{0.09}$. The addition of a small amount of iron to cobalt stabilizes the fcc phase and avoids the difficulties associated with the faulted structure that according to James,⁷ is typical of the hexagonal phase. On the other hand, the charge density of this alloy should be practically the same as that of pure fcc cobalt.

EXPERIMENT

Two single crystals in the shape of thin slabs approximately 40 and 30 μm thick were obtained by hand grinding from an ingot that, according to chemical analysis, had the composition: Co 91 at.%, Fe 9 at.%. After careful chemical polishing, the crystals were examined by a series of Laue photographs, which showed no polycrystalline layer. As a check of the chemical composition of the samples, the lattice parameter of the alloy was measured on a Philips 114.83-mm camera. The measured parameter $3.5540 \pm 0.001 \text{ \AA}$ confirmed within 1% the chemical analysis. The measurements were performed using Ag $K\alpha$ radiation monochromated by a singly bent LiF crystal. The x-ray tube was operated at 44 kV to prevent any second-order contamination. The incident beam consisted of α_1 and α_2 components in the ratio of approximately 3:1. By means of two pinholes, the incident beam divergence was collimated to 3 minutes of arc, a factor of 3 less than the smallest halfwidth observed. The reflections (111) and (200) were measured with an incident beam power of ap-

proximately 8000 counts/sec. The total circuitry dead time ($1.8 \pm 0.2 \mu\text{sec}$) and the attenuation factor of a Pd absorber (~ 2.5) were carefully measured before and after the experiment by the multiple foil technique. For the reflection pair (333)-(511), a much stronger beam was used. The integrated intensities of the reflection pair were corrected for sample thickness and incident beam power. Both factors showed a maximum variation of $\pm 1\%$. The mis-cut effect was eliminated in all cases by performing on each point two measurements with the crystal rotated by 180° . The mass absorption coefficient was calculated starting from the values measured by Cooper,⁸ and the sample density was obtained from the measured lattice parameter. For the elastic constants and the Debye temperature, the values obtained by Shapiro and Moss⁹ from the phonon dispersion curves were used. The integrated intensities of the (111) and (200) reflections were corrected for TDS using the Nilsson correction,¹⁰ as revised by Walker and Chipman.¹¹ The polarization factor corresponding to an ideally imperfect monochromator was used. Other details concerning the measurements and the procedure to correct for secondary extinction have been published previously.⁴

RESULTS AND DISCUSSION

The ranges of TDS and secondary extinction corrections for the (111) and (200) reflections are listed in Table I. The experimental values of the (111) and (200) scattering factors obtained from the measured structure factors applying the dispersion corrections calculated by Cromer and Liberman¹² are shown in Figs. 1 and 2 plotted as a function of T/Δ , where T is the crystal thickness and Δ is the reflection half-width. As in a previous experiment on Fe,⁵ this choice of variables is the one that best linearizes the experimental data. The linearly extrapolated values with their standard errors obtained from the fitting procedure, the free atom values calculated by Doyle and Turner,¹³ and the crystal-to-free-atom ratios are listed in Table II. Also listed is the ratio of the squares of the structure factors for the (333)-(511) pair and the t_{2g} percentage obtained with the following choice of parameters: $n_{3d} = 8$; $J_4(\text{Co}^*)$

TABLE I. Ranges of the TDS and secondary extinction corrections for the (111) and (200) reflections.

(<i>hkl</i>)	TDS (%)	Secondary extinction (%)
(111)	0.29-0.44	1.9-9.9
(200)	0.36-0.61	0.8-4.4

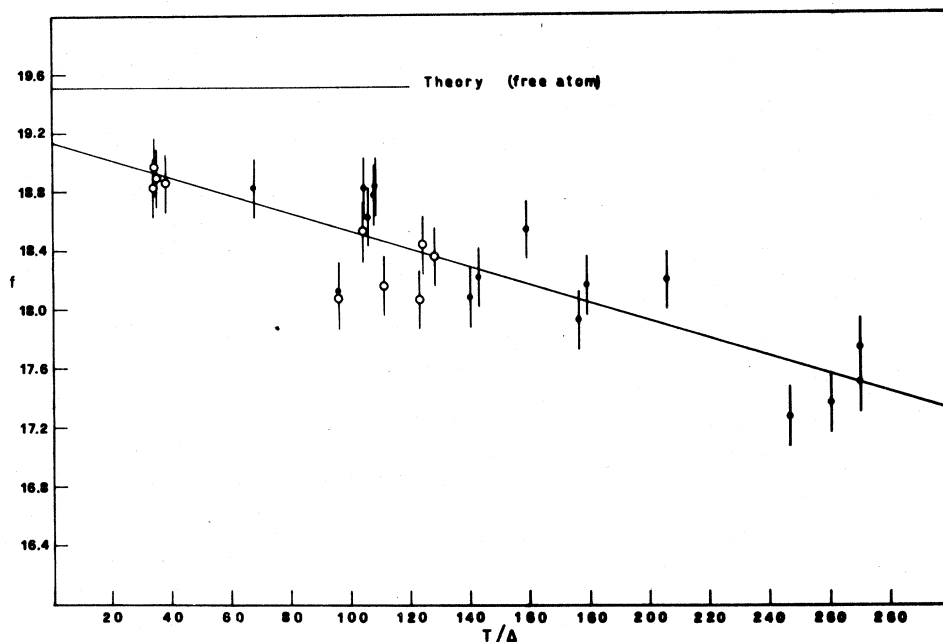


FIG. 1. Atomic-scattering factors measured from the (111) reflection are shown as a function of T/Δ . The solid line is the least-squares straight-line fit. The standard errors obtained from the fitting procedure are indicated. Open circles and dots denote the values obtained from crystals of thickness 30 and 40 μm , respectively.

$= J_4(\text{Fe}^+) = 0.085$. The values for J_4 were obtained from the calculations of Watson and Freeman¹⁴: the singly ionized state was chosen to approximate the $3d^{n-1}4s$ situation, presumably present in the solid. The t_{2g} percentage obtained from this experiment can be compared with that measured by the polarized-neutron technique¹⁵ if this alloy is considered to be a strong ferromagnet, that is, having the spin-up band entirely filled. The t_{2g} percentage (53) of the unpaired d electrons converted to the t_{2g} percentage of the total d charge gives a value comprised between 61 and 62, confirming, therefore, the slight anisotropy of total d charge of this alloy as measured in this experiment. On the contrary, the magnetic form factor of pure hcp cobalt has been measured¹⁶ to be al-

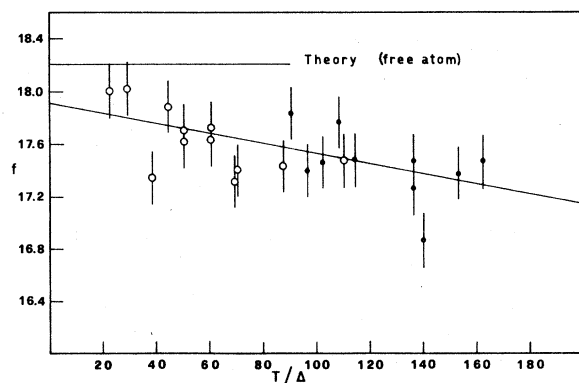


FIG. 2. Same as in Fig. 1 for the (200) reflection.

most perfectly spherical. Although it would be tempting to say that the addition of iron is at the origin of this difference, it is also possible that the structural change may play a significant role in this connection.

These results show an overall similarity to those obtained for nickel⁴ (if this is adjusted with the Cromer and Liberman dispersion corrections). For both metals the crystal scattering factor is, for the first two reflections, about 2% lower than the free-atom value calculated by Doyle and Turner. For what concerns charge-density asphericity, the agreement of x-ray and neutron results points to a small but detectable amount of anisotropy in the present alloy, while in the case of Ni, evidence of anisotropy has been obtained only by neutron scattering¹⁷ (t_{2g} percentage of unpaired electrons: 81, corresponding to 59% t_{2g} of the total charge). Listed below are the measured t_{2g} percentages of the total d charge from V to Ni which seem to show a break between body-centered and close-packed structures:

TABLE II. X-ray scattering factors of $\text{Co}_{0.91}\text{Fe}_{0.09}$. The free-atom values are those calculated in Ref. 13. Parameters used to evaluate the scattering factors are: $\lambda = 0.5605 \text{ \AA}$, $\mu = 182.2 \text{ cm}^{-1}$, $B = 0.446 \text{ \AA}^2$, $\Delta f' = 0.255$, $\Delta f'' = 0.62$.

(hkl)	f_{atomic}	f_{crystal}	$f_{\text{crystal}}/f_{\text{atomic}}$
(111)	19.49	19.15 ± 0.10	0.982
(200)	18.215	17.91 ± 0.11	0.983

$F_{(333)}^2/F_{(511)}^2 = 1.008 \pm 0.006$; $\%t_{g2} = 61.5$

V: 76%

Cr: 72%

Fe: 69%

Co_{0.91}Fe_{0.09}: 61.5%

Co(hex): spherical

Ni: 59%.

-
- ¹P. Suortti and L. D. Jemings, *Acta Crystallogr. A* **33**, 1012 (1977).
- ²J. J. DeMarco, M. Diana, and G. Mazzone, *Philos. Mag.* **16**, 1303 (1967).
- ³W. H. Zachariasen, *Theory of X-Ray Diffraction in Crystals* (Wiley, New York, 1945), Chap. IV.
- ⁴M. Diana, G. Mazzone, and J. J. De Marco, *Phys. Rev.* **187**, 973 (1969).
- ⁵M. Diana and G. Mazzone, *Phys. Rev. B* **9**, 3898 (1974).
- ⁶R. J. Weiss and J. J. De Marco, *Phys. Rev.* **140**, A1223 (1965).
- ⁷R. W. James, *The Optical Principles of the Diffraction of X-Rays* (Bell, London, 1958), Chap. X.
- ⁸M. J. Cooper, *Acta Crystallogr.* **18**, 813 (1965).
- ⁹S. M. Shapiro and S. C. Moss, *Phys. Rev. B* **15**, 2726 (1977).
- ¹⁰N. Nilsson, *Ark. Fys.* **12**, 247 (1957).
- ¹¹C. B. Walker and D. R. Chipman, *Acta Crystallogr. A* **25**, 395 (1969).
- ¹²D. T. Cromer and D. Liberman, *J. Chem. Phys.* **53**, 1891 (1970).
- ¹³P. A. Doyle and P. S. Turner, *Acta Crystallogr. A* **24**, 390 (1968).
- ¹⁴R. E. Watson and A. J. Freeman, *Acta Crystallogr.* **14**, 27 (1961).
- ¹⁵F. Menzinger and A. Paoletti, *Nuovo Cimento B* **10**, 565 (1972).
- ¹⁶R. M. Moon, *Phys. Rev.* **136**, A195 (1964).
- ¹⁷H. A. Mook, *Phys. Rev.* **148**, 495 (1966).