

X-ray scattering factor of 3d metals. A comparison between theory and experiment

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(Received 18 August 1980)

The absolute measurement with Ag $K\alpha$ radiation of the scattering factor at the first reflection of 3d metals from V to Ni, using imperfect single crystals, has been completed. The x-ray results have been compared with those obtained from critical voltage experiments and with free-atom and solid-state calculations. The scattering factors measured with x rays appear to be affected by 1–2 % residual extinction. Band-calculated and experimental critical voltage values are in agreement within ~ 0.5 –1 %. The difference between free-atom and crystal values is of the order of 1% with the exception of Cr and Cu, whose peculiar behavior is due mainly to their free-atom configuration. Starting from Cr, band effects on crystal scattering factors tend to decrease with the filling of the 3d band.

INTRODUCTION

In order to obtain quantitative information about solid-state effects on charge distribution, several accurate x-ray measurements of the scattering factor of 3d metals have been performed. Although all experimental crystal values have been reported to be lower than those calculated self-consistently for the corresponding free atoms,¹ different measurements for the same metal have often resulted in conflicting values, ranging, in the worst cases and for the first two or three reflections, from agreement with to 5–6 % less than free-atom values. This lack of reproducibility of x-ray measurements does not seem to depend on the technique used (powder or single crystal) as shown, for instance, by the fact that some results obtained with powders exhibit a variation well beyond the stated accuracy of each measurement. The situation is further obscured by the fact that a set of scattering factors representative of all 3d metals and obtained with the same technique of measurement and the same procedure of sample preparation has not yet been reported.

Notwithstanding these difficulties, Diana and Mazzone² have suggested that the experimental scattering factor for the first reflection, starting from Cr which has been measured to be $\sim 5\%$ low, approaches free-atom values as the number of 3d electrons is increased. This statement is difficult to reconcile with the fact that the (110) scattering factor of V has been independently measured^{3,4} to be only $\sim 1\%$ low. In conclusion, these contradictions and uncertainties have cast significant doubts on most x-ray results which, therefore, have been of limited help also as a guide for theoretical solid-state calculations.

Severe difficulties in fact occur also on the theoretical side of the problem, since band calculations cannot be performed starting from first principles, but rely, in the majority of cases, upon the choice of an effective one-electron potential

capable of accounting for most of the many-electron exchange and correlation effects. In the framework of the currently adopted $X\alpha$ method, for instance, the calculated scattering factors are not only dependent on the value of α (the parameter which accounts statistically for exchange interaction), but since it has been found that the use of a different potential for the t_{2g} and e_g states improves the agreement between theory and experiment in several phenomena related to the shape of the Fermi surface, it has been stated^{5,6} that such a potential should also be used for scattering factor calculations. As a result, band-theoretical values for the same metal in some cases differ by an amount which is of the same order of magnitude of the solid-state effect which one is trying to measure. This being the case, it is difficult, without considering other experimental work, to perform an objective choice among the existing x-ray and theoretical data in order to reach a reasonably accurate conclusion as to the extent of charge redistribution in 3d metals.

Accurate values of the x-ray scattering factor for the first few reflections can also be obtained by electron diffraction with the critical voltage method^{7,8,9} (CVM in what follows). With very few exceptions CVM results for 3d metals are about 1% below free-atom theory. Since this method is supposed to have lesser uncertainties than x-ray elastic scattering has, we have decided to complete the measurement, with Ag $K\alpha$, of the first reflection of the metals V to Ni (excepting Mn) using imperfect single crystals, in order to have a homogeneous set of x-ray results to compare with CVM experiments. To this purpose we have measured with Ag $K\alpha$ the (110) scattering factor of Cr and Fe. It was also hoped that this experiment would help to explain the results of a measurement with Ag $K\alpha$ of the (110) scattering factor of a $\text{Fe}_{0.76}\text{Cr}_{0.24}$ alloy. The result of this measurement will be reported in what follows, together with those of the pure metals.

The main source of error in an imperfect single-crystal measurement, once secondary extinction has been corrected according to the method described by De Marco,¹⁰ is due to primary extinction. In order to reduce the influence of this effect, an extrapolation procedure to infinite peak half-width and the use of as short a wavelength as possible (compatible with the avoidance of multiple Bragg scattering), seem to be the two most effective means, although it is almost impossible to estimate the residual error and to choose the best extrapolation function.¹¹ One of the results of a comparison between x rays and CVM, therefore, would also be the possibility to estimate the amount of residual extinction in imperfect single-crystal experiments and to check the validity of the procedure adopted in order to account for this unwanted effect.

EXPERIMENT

Several single crystals in the shape of thin slabs were obtained by hand grinding from ingots of Fe, Cr, and an FeCr alloy which, according to chemical analysis, had the composition: Fe 76 at.%, Cr 24 at.%. As a check of the composition of the alloy, the lattice parameter was measured on a Philips 114.83-mm camera. The measured parameter 3.8722 (2) Å, confirmed within 2% the chemical analysis. The measurements were performed in symmetrical transmission with Ag K α radiation monochromated by a singly bent LiF crystal. The miscut 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,¹² using in all cases the x-ray density. For the Debye temperature of Fe (424 K) and Fe_{0.76}Cr_{0.24} (420 K), the values measured by Shirley *et al.*¹³ were used. For Cr, an average (510 K) of several values reported in the recent literature was used. The uncertainty on the measured f^2 's resulting from a variation of the Debye temperatures of 15 K was practically negligible (~0.1%). All the measured intensities were corrected for thermal diffuse scattering (TDS) according to Nilsson.¹⁴ The correction ranged from ~0.2 to 0.4%. For the FeCr alloy a weighted average of the elastic constants of the pure metals was used. Since all crystals were pressed between two polished steel plates in order to increase mosaic spread, particular care was used to eliminate any polycrystalline layer by chemical (electrochemical in the case of Cr) polishing. Mounting the samples on a conventional diffractometer it was possible to check that no detectable Debye-Scherrer halo was present. The background value for the Fe and Cr

samples was compared with that of the corresponding single crystals used previously.^{2,15} While in the case of Cr the two values were very similar, in the case of Fe it was found that the background of the old crystal was higher by a factor of 3. Chemical polishing of the old crystal (whose thickness was, within 10%, the same of the new one) reduced the background to practically the same value of the new crystal (this point will be discussed further on). A few measurements were then made also on the old Fe crystal. The number of measurements which has been performed is as follows: 24 on FeCr crystal A and 22 on FeCr crystal B ($\mu t \sim 1$ for both crystals); 24 on Cr crystal A ($\mu t \sim 1.2$) and 6 on Cr crystal B ($\mu t \sim 0.6$); 20 on the new Fe crystal and 4 on the old Fe crystal ($\mu t \sim 0.7$ for both crystals). Other details relative to x-ray beam, instrumentation, polarization factor, dead-time correction, and the procedure to correct for secondary extinction have been published previously.^{2,11}

RESULTS AND DISCUSSION

The values of the (110) scattering factor obtained from an extrapolation to infinite peak half-width of the measured structure factors and with the use of the Cromer and Liberman¹⁶ dispersion correction, are collected in Table I. Separate extrapolations of the two FeCr crystals gave results differing by 0.5%. All quoted errors represent the standard errors of the extrapolated values obtained from the fitting procedure. If the Cr percentage of the alloy is decreased by 2%, the quoted scattering factor should be increased by 0.3% and the ratio $f_{\text{crystal}}/f_{\text{atom}}$ by 0.1%. This ratio, therefore, is practically insensitive to small variations of composition. No correction for size effects, as discussed by Borie,¹⁷ has been made since the factor $2M'$ is, for this alloy, absolutely negligible ($\sim 10^{-4}$). It is immediately seen that while the present Cr scattering factor is not very different from that obtained with Mo radiation¹⁵ if adjusted with the dispersion correction of Ref. 16, the present result for Fe is very different from that obtained previously.² This difference is caused by the excessively high background level of

TABLE I. The (110) scattering factor of Cr, Fe, and Fe_{0.76}Cr_{0.24}.

	f_{atom}	f_{crystal}	$\frac{f_{\text{crystal}}}{f_{\text{atom}}}$
Cr	16.72	16.00 ± 0.25	0.957
Fe	18.46	18.06 ± 0.20	0.978
Fe _{0.76} Cr _{0.24}	18.05	17.72 ± 0.10	0.981

the old crystal, as confirmed by the fact that after this crystal was chemically polished, the results of four measurements were higher than any of those obtained before and perfectly compatible with those of the new Fe crystal.

In order to visualize the results obtained with Ag radiation, the ratio $R = f_{\text{crystal}} / f_{\text{atom}}$ for the first reflection, corresponding to a value of $\sin\theta/\lambda \sim 0.24$, has been plotted as a function of atomic number in Fig. 1. Also shown in the same figure are the values of R obtained for Cr, Fe, and Ni with Mo radiation and the values of R obtained from CVM experiments with their errors. For better clarity, error bars for x-ray values have not been indicated; it may be sufficient to say that they are larger, even by a factor of two in the worst cases, than those of CVM and that x-ray upper limits are practically coincident with CVM lower limits. A comparison between the two sets shows that Ag radiation results are lower than the corresponding CVM ones by 1–2% and that Mo radiation results for Cr and Ni are about 1% lower than those obtained with Ag. It is also seen that the value of R for the FeCr alloy is very similar to that of pure Fe. If, however, the result of the alloy had been compared with the results of the pure metals obtained with Mo radiation, it would have been inexplicably high (~3%). Although the CVM and x-ray results are not incompatible, the regular occurrence of a difference between the two sets and the difference between Ag radiation and Mo radiation results for Cr and Ni, point to a

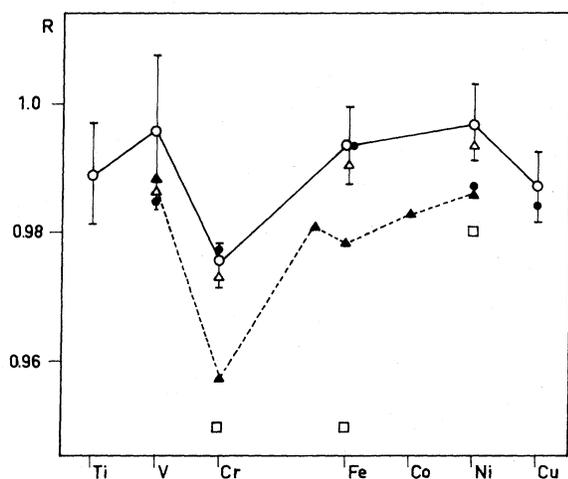


FIG. 1. The ratio $R = f_{\text{crystal}} / f_{\text{atom}}$ at the first reflection. Circles and solid line refer to CVM values; solid triangles and broken line to Ag radiation x-ray values; squares to Mo radiation x-ray values; open triangles to band-theoretical values of Callaway and co-workers; dots to band-theoretical values of Wakoh and co-workers. Error bars are relative to CVM values.

residual λ -dependent systematical error in the scattering factors obtained with x rays, which can be attributed to residual extinction.

For what concerns the variation of R with atomic number, it is possible to observe that both sets of data show, for Cr, a percent difference between crystal and free-atom two or three times as large as for the other metals. Since this difference is, again, not much beyond experimental errors, we have also plotted in Fig. 1 the values of R obtained from the only existing fairly complete sets of band-theoretical scattering factors, that is those calculated by Wakoh and co-workers^{6,18} and by Callaway and co-workers.¹⁹ Within the local potential approximation, Callaway's calculations can be considered as accurate as possible at least at the present state of the art. The two sets of theoretical results differ among themselves and from CVM values by 0.5–1%, thus showing that these values are fairly well representative of the real crystal values. This concordance, moreover, strengthens the above conclusion concerning the existence of residual extinction in x-ray results. Particularly important is the fact that both sets of theoretical values show, at the Cr position, the same dip displayed by the experimental data, thus confirming the existence of this effect. We can, therefore, conclude that on passing from free-atom to crystal, there is a decrease of the scattering factor at the first reflection of the order of 1%, with the exception of Cr which shows a decrease two or three times as large. Other differences among remaining metals are not sufficiently clear to be identified with any reasonable certainty from Fig. 1, and will be analyzed later.

In order to understand the reason of the peculiar behavior of Cr, it is instructive to plot separately, at $\sin\theta/\lambda = 0.24$, the two quantities which define R , that is f_{crystal} and f_{atom} , as functions of atomic number Z . In particular, in order to have two slowly-varying almost linear functions of Z , it is convenient to plot $f'_{\text{crystal}} = f_{\text{crystal}} / Z$ and $f'_{\text{atom}} = f_{\text{atom}} / Z$. These two quantities are shown in Fig. 2. For what concerns f'_{atom} , which has been calculated from the data of Ref. 1, one has that all points lie on a straight line with the exception of Cr and Cu which are about 1% above the values obtained from a linear interpolation. This feature is present, in the values of Ref. 1, in the interval $0 < \sin\theta/\lambda < \sim 0.35$ and arises from the fact that free-atom values of Cr and Cu are calculated for the configuration $3d^{n-1}4s$ while all other elements have the configuration $3d^{n-2}4s^2$. The difference introduced by the change of configuration can also be observed in the free-atom values calculated by Freeman and Watson,²⁰ who report the scattering factors of Cr and Cu in both configurations. It

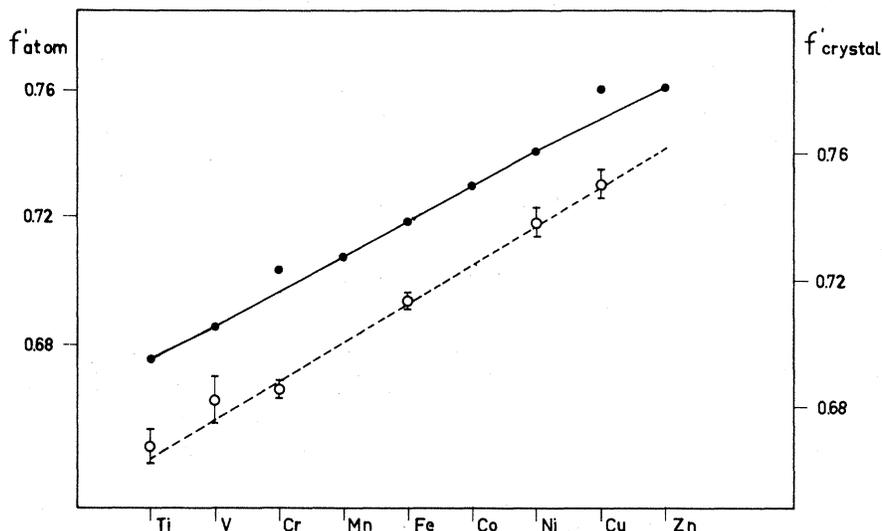


FIG. 2. The ratios $f'_{crystal} = f_{crystal}/Z$ and $f'_{atom} = f_{atom}/Z$ at $\sin\theta/\lambda = 0.24$. Dots and continuous line refer to f'_{atom} , circles and broken line to $f'_{crystal}$. The broken line is the best least-squares straight-line fit through the circles. The f'_{atom} scale (to the left) is displaced with respect to the $f'_{crystal}$ scale (to the right).

should be remarked that this behavior has nothing to do with the fact that Cr and Cu have a full or semifull d shell (as evidenced by the fact that Mn and Zn have the same number of $3d$ electrons as Cr and Cu but a regular value of f'_{atom}), but depends on the fact that the scattering function for a $3d$ electron is higher than for a $4s$.

For what concerns $f'_{crystal}$ we have plotted in Fig. 2 the values obtained by CVM (adjusted to $\sin\theta/\lambda = 0.24$ with a small correction calculated on the basis of free-atom values). The experimental points are described, within the errors, by a straight line. Shown in Fig. 1 is the best least-squares straight-line fit. From these observations we can conclude that the dip displayed by Cr in Fig. 1 arises mainly from the fact that its value of f'_{atom} is higher than that which would be obtained interpolating from neighboring elements. If this is true, then we expect that a similar dip should be displayed also by Cu. Inspection of Fig. 1 shows that, indeed, there is a slight decrease of R going from Ni to Cu, but this difference is so small that the existence of a dip for Cu cannot be inferred with reasonable certainty from the data of Fig. 1 alone, especially since no value of R for Zn is available. An indication that a dip at the position of Cu does indeed exist can be obtained observing another effect displayed by the curves of Fig. 2, namely that the slope of $f'_{crystal}$ is higher than that of f'_{atom} in such a way that the two curves tend to the same value at $Z = 30$. If, as a consequence, the value of R for Zn is put equal to 1, then the existence of a dip for Cu becomes almost as evident as for Cr.

The considerations presented so far have been relative to the scattering factor at the first reflection. For what concerns higher reflections, available data are scantier and it is not possible to analyze them at the same level of detail. Nonetheless it is possible to say that, if the present analysis is correct, one expects that the values of R for V, Cr, and Fe at the (200) reflection, that is, at $\sin\theta/\lambda \sim 0.34$, should display a much more regular behavior than at $\sin\theta/\lambda = 0.24$. Experimental (CVM) and band-theoretical data for the (200) reflection are presented in Table II. It is possible to see that the difference between crystal and free-atom values is smaller than for the (110) reflection and that there is almost no difference in the value of R for the three metals. We can summarize this part of the discussion stating that, at the first reflection, in addition to the effect of free-atom configuration on R , there is a small ($\sim 1\%$) solid-state effect on the scattering factor which decreases with the filling of the d band, at least in the second part of it. This trend is consis-

TABLE II. The ratio $f_{crystal}/f_{atom}$ for the (200) reflection of V, Cr, and Fe. CVM = Ref. 9; W = Refs. 6, 18; C = Ref. 19. The free-atom values are those of Ref. 1.

	V	Cr	Fe
CVM	1.00 ± 0.013	0.990 ± 0.008	0.995 ± 0.005
W	0.993	0.990	0.991
C	0.992	0.979	0.988

tent with the known radial behavior of $3d$ wave functions at the bottom and at the top of the d band. The size of this effect, however, is such as to make impossible a detailed description of it, at least at the present level of accuracy of experiments and calculations. The difference between crystal and free-atom values decreases with increasing $\sin\theta/\lambda$ and is barely noticeable at $\sin\theta/\lambda = 0.34$. The difference $\sim 5\%$ observed in some x-ray experiments is, therefore, to be mainly attributed to extinction in the case of imperfect single crystals and to a number of factors, described in detail by Suortti and Jennings,²¹ in the case of powders.

CONCLUSION

Although the present analysis describes the main features of the scattering factor of $3d$ metals, it seems that in order to obtain a really accurate picture of the details of charge redistribution in these solids, it would be necessary to know the scattering factor of each metal at several values of $\sin\theta/\lambda$ with an accuracy of the order 0.1% . Such an accuracy over an extended range of $\sin\theta/\lambda$ is, probably, beyond the present possibilities of x-ray scattering and, also, of electron diffraction. In particular, the angular behavior of charge density can be studied only at those relatively high values of $\sin\theta/\lambda$, where the aspherical part of the charge density gives a detectable contribution to the total scattering factor. While

several, although partial, x-ray studies of charge density asphericity have been reported, for what concerns CVM experiments we have that, in addition to the necessity of knowing all the Fourier coefficients V_n of the reflections ($nh\ nk\ nl$), prohibitively high values of accelerating voltage would be required.

Anyway, some points seem to be reasonably certain even at the present stage: Scattering factors obtained by means of x-ray diffraction from imperfect single crystals are affected by a residual extinction of the order of $1-2\%$, even when measured with Ag radiation; CMV and the most accurate band-theoretical values are in agreement well within experimental errors; the scattering factor of $3d$ metals at the first reflection is lower than that of corresponding free-atoms by a small amount which is of the order of 1% (with the exception of Cr and very probably Cu); the peculiar behavior of Cr and Cu is due to a large extent to their free-atom configuration; the difference between crystal and free atom tends to decrease with the filling of the d band, at least in the second part of the $3d$ series; t_{2g} states are favored over e_g states in the case of bcc metals, while close-packed ones appear to be more nearly spherically symmetric.¹¹

ACKNOWLEDGMENT

I want to thank Dr. F. Sacchetti for many stimulating discussions and helpful suggestions.

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