X-RAY MEASUREMENT OF THE DISTRIBUTION OF ELECTRONS IN IRON AND COPPER

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In a recent publication Weiss and DeMarco[1] have reported an x-ray measurement of the number of $3d$ electrons in the metals Cr, Fe, Co, Ni, and Cu. Their results indicate that the metals with body-centered cubic structures have outer electron distributions which depart considerably from atomic $3d$ states. This letter communicates briefly the results of some present measurements of the atomic scattering factors of iron and copper which are not in agreement with Weiss and DeMarco.

The atomic scattering factors were obtained from the integrated intensities of Bragg reflections of copper and iron. One of the most important considerations in the x-ray measurement of scattering factors is the correction for extinction. There is at present no reliable theoretical method to correct for extinction. Hence, to make an accurate measure of scattering factors, one should perform the experiment in such a manner as to render extinction effects negligible. There is good evidence[2,3] that in a cold-worked metal, extinction effects can be made negligible, and therefore the atomic scattering factors were measured with cold-worked powders of iron and copper.

X-ray intensities were measured with monochromatic Fe K_α radiation. Carbonyl iron and electrolytic copper powders with a particle size 3-5μ in diameter were pressed into briquets in a highly polished mold with pressures ranging from zero to 60 000 lb/in.^{2}. At the higher pressures, the powders deformed plastically, and the copper briquets had a mirror surface with about a 3μ variation in flatness, estimated microscopically. The integrated intensities of corresponding reflections from all specimens agreed to within 6%. This includes specimens held together only by a bonding agent and those pressed with 60 000 lb/in.^{2}. As the molding pressure was increased, the half-width of the reflections increased, and the α_1-α_2 doublet resolution decreased. This indicates that the degree of cold work increased with increased molding pressure. Loose powders cold-worked in a small oscillating ball mill before being pressed into briquets gave intensities for all reflections within the 6% spread. Although there was considerable variation in the surface roughness of the different specimens, the variation in intensity was within experimental error.

The intensities of the five copper reflections relative to one another agreed to within 5% of the expected theoretical ratios. Similarly, the four measured iron reflections were also found to be internally consistent. This agreement shows that extinction and surface roughness are negligible for these powders under these experimental conditions. To put the iron and copper intensities on an absolute basis, the intensities from a finely pulverized rock salt specimen were measured under the same conditions as the metal powders. Using the tabulated atomic scattering factors for Na^+ [4] and Cl^-,[5] a parameter which effectively measures the primary beam intensity can be calculated. Knowing the primary beam intensity, an experimental value for the atomic scattering factors for copper and iron can be calculated from the observed intensities. These results are given in Table I,

Table I. Measured values of the atomic scattering factors for iron and copper standardized against sodium chloride.

	NaCl			Copper			Iron	
hkl	Fitted	Theory[a, b]	*hkl*	Observed	Theory[b]	*hkl*	Observed	Theory[c]
200	23.0	21.47	111	22.5	22.16	110	19.3	18.77
220	18.4	18.21	200	20.6	20.78	200	15.8	15.57
222	15.9	16.17	220	17.0	16.78	211	14.0	13.45
400	15.2	14.76	311	15.1	14.76	220	12.3	11.91
420	13.2	13.70	222	14.9	14.20			
422	12.8	12.85						

[a] See reference 4. [b] See reference 5. [c] See reference 6.

together with the theoretical f_{Cu}[5] and f_{Fe}.[6] The experimental f values for NaCl obtained from the intensity parameter are also included. The (110) reflection of iron and the (111) of copper were carefully measured for three different pairs of specimens. Assuming $f_{(111)}$ of Cu[4, 5] to be 22.16 (the value calculated from free-atom wave functions), the measured values of $f_{(110)}$ of iron are in the range 18.9 ± 0.1.

The dispersion corrections for Fe K_α radiation were calculated from Parratt and Hempstead[7] and are $\Delta f' = -2.45$ for iron and $\Delta f' = -1.51$ for copper. (The imaginary part, $\Delta f''$, has a negligible contribution.) To provide a cross check on the dispersion corrections, the iron (110) and copper (111) reflections were measured with unfiltered molybdenum radiation for which the correction is small and of opposite sign to that for iron radiation. Two pairs of specimens gave 18.8 and 18.9 for $f_{(110)}$ of iron relative to copper. These are in good agreement with the Fe K_α results.

Considering the consistent internal agreement with theory of all the measured reflections of either iron or copper and the external agreement with the rock salt intensities, it is felt that the validity of the assumptions of negligible extinction and surface roughness absorption has been demonstrated.

Using the calculated free-atom scattering factors for copper and sodium chloride, the value of f for iron at $\sin\theta/\lambda = 0.247$ [the (110) reflection] is estimated at 18.9 ± 0.2 relative to copper and 19.3 ± 0.6 relative to NaCl, while the free-atom calculation[6] gives 18.77. Thus, one may conclude that within experimental error the observed scattering factor for iron agrees with that calculated from the wave functions of the free atom.

If one chooses to ascribe any difference between observed and theoretical f to an excess or deficiency of $3d$ electrons, this may be done as follows: The contribution of each iron $3d$ electron to f at $\sin\theta/\lambda = 0.247$ is very nearly 0.60 unit.[6] Hence, in terms of these electrons, iron has 6.2 ± 0.4 $3d$ electrons relative to copper and 6.9 ± 1.0 relative to NaCl. Similarly, the contribution of each copper $3d$ electron to $\sin\theta/\lambda = 0.240$ [the (111) reflection] is approximately 0.62.[1] The measured value of $f_{(111)}$ of copper relative to NaCl is 22.5 ± 0.6 (free-atom value $= 22.16$), which, in terms of $3d$ electrons, is 10.5 ± 1.0.

Taking into account the estimated experimental errors, it is concluded that, to an accuracy of about one $3d$ electron, the number of electrons in metallic iron and copper is not different from that in the free atom. This contrasts with the value of (2.3 ± 0.3) $3d$ electrons for iron reported by Weiss and DeMarco from single-crystal measurements.

A more detailed report will be submitted shortly to the Physical Review.

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ELECTRON EMISSION FROM BREAKDOWN REGIONS IN SiC *p-n* JUNCTIONS

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We have measured electron emission currents from reverse-biased *p-n* junctions in SiC. In 20 samples the maximum emission ranged from 10^{-12} amp to 10^{-6} amp. In each case the emission depended strongly on sample preparation. Best results were obtained by heating the sample at 270°C in vacuum for several hours.

Burton[1] has reported similar emission from a reverse-biased junction in Si, but only after the addition of cesium to the sample tube. Evidently the cesium depresses the Si work function enough to permit the escape of some of the energetic electrons known to be present during breakdown. The high energy gap of SiC ($E_G = 2.86$ ev)[2] ensures the presence of correspondingly high-energy electrons at breakdown (for impact ionization electron energies of about one and a half times the gap are necessary).[3] We therefore expect to have conduction band electrons with energies in the neighborhood of 4.3 ev, an amount