Metallic-Cu x-ray form factors

Alma Marcus Gray
Physical Science Division, Watervliet Arsenal, Watervliet, New York 12189
(Received 18 July 1973)

Two sets of experimental Cu x-ray form factors are compared for consistency in terms of a simple charge-distribution model. The results of Temkin, Henrich, and Raccah fit the model very well, while those of Hosoya and Yamagishi do not give a satisfactory fit.

Experimental Cu x-ray form factors of Temkin, Henrich, and Raccah[1] (THR) and of Hosoya and Yamagishi[2] (HY) are compared for their consistency. A simple parametrized model for the electronic charge distribution in cubic crystals and the corresponding parametrized form-factor expression were derived in an earlier publication.[3] The model consists of a superposition of slightly distorted theoretical atomic charge distributions. The parametrized-form-factor expression is fitted to the set of measured form factors by a least-squares technique; the standard deviation is taken to be a measure of the consistency of the data.

The atomic charge distribution was generated from Mann's Hartree-Fock (HF) atomic wave functions.[4] Atomic form factors calculated from these were found to agree within a ± 0.02 with HF form factors of Cromer and Mann[5] listed in Table III of Ref. 1. Relativistic wave functions were not used because the higher-order THR reflections approximate more closely to the nonrelativistic form factors.

The form-factor expression of Ref. 3, with three independent parameters a_0, b_1, and b_2, was fitted to two different models. In one the $3d^{10}4s^1$ electron distribution was allowed to vary, in the other only the $4s^1$ distribution. In the former case only a_0 was found to have significance, in the latter a_0 and b_1 were found to be significant in fitting to the THR data. Results are shown in Table I. The best fit was obtained by varying only the $4s^1$ charge distribution. The result indicates an outward flow of electronic charge from the nuclear regions exceeding the atomic $4s^1$ charge density there, also a reduction in symmetry of the "atom" from spherical to cubic. The HY form factors could not be fitted in a satisfactory manner, the deviation in $f(220)$ exceeding the possible error.

Comparison of the band-structure results listed in Table IV of Ref. 1 with the THR form factors shows that the Snow $\alpha = \frac{2}{3}$ and the Wakoh $\alpha = 1$ calculations give the best over-all agreement, however, neither one fits $f(111)$ within the experimental error. Both calculations were performed with pure Slater exchange and self-consistency, Snow using the augmented-plane-wave (APW) and Wakoh the Green's-function method. Wakoh obtained much better agreement with the THR form factors. If the reason for this could be determined our understanding of band-structure calculations might be improved.

Summarizing, it was found, by fitting a model

TABLE I. Consistency of two sets of experimental x-ray form factors for Cu. Empirical confidence bounds on fitted values are shown in parentheses. All data for $T = 0\,^{\circ}\mathrm{K}$. $D = 28.00 a_B$ for the model charge-density cut-off value.

		Form Factor				
		Fit			Fit	
hkl	Expt. THR	$3d^{10}4s^1$ (a_0)	$4s^1$ (a_0, b_1)	Expt. HY	$3d^{10}4s^1$ (a_0)	$4s^1$ (a_0, b_1)
111	21.93 ± 0.15	12.91 (0.04)	21.94 (0.02)	22.02 ± 0.09	22.08 (0.06)	22.02 (0.12)
200	20.36 ± 0.15	20.55 (0.04)	20.36 (0.03)	20.62 ± 0.18	20.72 (0.05)	20.65 (0.11)
220	16.70 ± 0.16	16.63 (0.04)	16.72 (0.00)	16.99 ± 0.13	16.77[a] (0.04)	16.75[a] (0.04)
311	14.71 ± 0.17	14.64 (0.03)	14.71 (0.00)	14.79 ± 0.09	14.20 (0.03)	14.73 (0.03)
222	14.18 ± 0.17	14.09 (0.03)	14.12 (0.01)	14.23 ± 0.09	14.75 (0.03)	14.17 (0.03)
400	12.33 ± 0.20	12.33 (0.02)	12.35 (0.01)	12.28 ± 0.45	12.41 (0.03)	12.38 (0.06)
Standard deviation		0.094	0.028		0.11	0.11
a_0		0.935 (0.018)	−15.4 (1.7)		1.00 (0.02)	−4.2 (7.5)
a_1 (a_0, b_1) a_B^{-1}		0.061 (0.016)	8.2 (0.7)		0.00 (0.02)	2.2 (2.9)
a_2 (a_0, b_1) a_B^{-2}		−0.0034 (0.0006)	−0.27 (0.02)		−0.0012 (0.000)	−0.07 (0.09)
b_1 a_B^{-1}			−0.308 (0.006)			0 (67)

[a]Exceeds error bounds.

crystal charge distribution to the THR experimental x-ray form factors, that the electron distribution for metallic Cu can be reproduced by a superposition of "atoms" with a slight redistribution of atomic charge. The symmetry of the lattice must be satisfied for every proposed model, however, a different radial dependence could be postulated. The success of our particular model in *predicting*[3,6] (i.e., without fitting to them) magnitudes of *forbidden* structure factors of Si in good agreement with experimental values supports its plausibility. The HY experimental results could not be fitted by our particular model. Because this model seems physically plausible the THR set of form factors appears preferable to the HY set as a standard for band-structure calculations. The band-structure charge distribution should be changed so as to give better agreement with the measured $f(111)$ form factor.

---

[1]R. J. Temkin, V. E. Henrich, and P. M. Raccah, Phys. Rev. B 6, 3572 (1972).
[2]S. Hosoya and T. Yamagishi, J. Phys. Soc. Jap. 21, 2638 (1966).
[3]A. Marcus Gray, Phys. Rev. B 5, 253 (1972).
[4]J. B. Mann (unpublished).
[5]D. T. Cromer and J. B. Mann, Acta Cryst. A 24, 321 (1968).
[6]A. M. Gray, Bull. Am. Phys. Soc. 18, 322 (1973); and unpublished.