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Absolute X-Ray Scattering Factors of Silicon and Germanium

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The absolute scattering factors of silicon and germanium were measured with x rays on perfect crystals. In both cases the results were consistent with a superposition of Hartree-Fock free-atom radial charge densities. This is to be contrasted with the metals aluminum, chromium, iron, and copper, which evidence marked expansion of the radial charge densities in the solid. The presence of the forbidden 222 reflection in silicon together with contributions to the low-angle reflections reveal that the angular part of the charge density points toward the four tetrahedrally disposed nearest neighbors.

I. INTRODUCTION

SEVERAL measurements of absolute x-ray scattering factors in the metals aluminum, iron, chromium, and copper[1,2] have shown departures of $\approx 5\%$ from the Hartree-Fock free-atom scattering factors[3] while the absolute x-ray scattering factors of the free atoms of neon, argon, krypton, and xenon[4] agree to better than $\approx 1\%$. In addition the absolute scattering factors of the semiconductor silicon[5] and the intermetallic compounds CoAl and NiAl[6] are in good agreement with Hartree-Fock free-atom values.[3] One might conclude from these results that the atoms of aluminum, iron, chromium, and copper undergo pronounced changes in electron charge density when these atoms become part of the metallic bond. If this is the case, then the x-ray technique can provide important clues to the understanding of the electronic structure of solids.

In order to provide further examples for comparison, we have measured the absolute scattering factors of silicon and germanium employing "perfect" crystals. This serves to double-check the former measurements on silicon which were performed on powder samples and, in addition, it adds the nonmetallic element germanium whose atomic number is not too far removed from iron, copper, and chromium. We can say at the outset that for both silicon and germanium good agreement with free-atom Hartree-Fock calculations was obtained.

II. EXPERIMENTAL TECHNIQUE

Two silicon crystals ([110],[111]) and two germanium crystals ([110],[111]) were employed, the [111] silicon crystal being dislocation- and oxygen-free (dislocation count by metallograph examination). It was assumed that the dislocation- and oxygen-free silicon crystal was sufficiently "perfect" so that the perfect crystal formula represented the integrated intensity to at least $\frac{1}{2}\%$. The [110] silicon crystal was not dislocation-free but a comparison of its (111) structure factor (measured in transmission) with the (111) structure factor of the dislocation-free crystal (measured in reflection) showed them to be identical for the Mo-$K\alpha$ radiation used.

The perfection of the [110] germanium crystal was checked by the internal consistency of the (220) structure factors taken in reflection and transmission. In the latter case the product of the absorption coefficient and crystal thickness exceeded 25 so that the integrated intensity in this anomalous transmission range was extremely sensitive to crystal perfection. No internal check of the [111] crystal was made, but both crystals came from the same source and the family of reflections (111), (333), (444), and (555) all gave good agreement with Hartree-Fock scattering factors, the outer reflections being particularly sensitive to structural imperfections.

The crystal surfaces were prepared by first lapping them in 600-grit SiC and then etching in 1 part HF and 3 parts HNO_3 until the integrated intensity attained its lowest value ($\approx$10-min etching time). The Mo-$K\alpha$ radiation was selected by a singly bent LiF crystal [200] in slit geometry with a beam divergence striking the sample of $\approx 0.05°$. Scintillation counters were employed for both monitor and detector and the counting rates were kept sufficiently low so that the dead-time corrections did not exceed $1\frac{1}{2}\%$. The x-ray tube potential was maintained at 31 kV so that no half-wave-length photons were excited. The measurements were placed on an absolute basis by determining the incident beam power through zirconium foil absorbers and the absorption coefficient of the silicon and germanium were measured through thinly ground slabs of the materials.

III. THE MEASUREMENTS

The equation relating the integrated intensity E of a perfect crystal to the structure factor F is

$$\frac{E\omega}{I}=\frac{K(e^2/mc^2)\lambda^2|F_H'|e^{-M}R_H{}^y(g,k,A)[1+\alpha\Gamma]}{\pi\sqrt{|b|}(V\sin 2\theta)}, \quad (1)$$

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[1] B. Batterman, D. Chipman, and J. DeMarco, Phys. Rev. **122**, 68 (1961); L. Jennings, D. Chipman, and J. DeMarco, Phys. Rev. **135**, A1612 (1964).

[2] M. J. Cooper, Phil. Mag. **7**, 2059 (1962).

[3] *International Tables for X-Ray Crystallography* (Kynoch Press, Birmingham, 1962), Vol. III, pp. 202–207.

[4] D. R. Chipman and L. D. Jennings, Phys. Rev. **132**, 728 (1963).

[5] S. Göttlicher and E. Wölfel, Z. Elektrochem. **63**, 891 (1959).

[6] M. J. Cooper, Phil. Mag. **8**, 811 (1963).

where ω is the angular velocity of the crystal, I the incident beam power (photons/sec), K the polarization factor, V the volume of the unit cell, $|F_H'|$ the real part of the structure factor, b the ratio of the direction cosines of the incident and emergent beams (γ_0 and γ_H, respectively) both taken relative to the crystal surface, $[1+\alpha\Gamma]$ the contribution of one phonon diffuse scattering to the integrated intensity, e^{-M} the Debye-Waller factor, and $R_H{}^y(g,k,A)$ the absorption factor, where for a crystal of thickness t,

$$g=-\frac{(1-b)\mu V(1+k^2)^{1/2}}{4\sqrt{|b|}\,(e^2/mc^2)\lambda|F_H|Ke^{-M}}\,, \qquad (2)$$

$$k=F_H''/F_H'\equiv\epsilon F_0''/F_H'\ , \qquad (3)$$

$$A=\frac{(e^2/mc^2)\lambda|F_H'|\,tKe^{-M}}{V|\gamma_0\gamma_H|^{1/2}}\,. \qquad (4)$$

Tables of values of $R_H{}^y$ (Bragg and Laue cases) as well as expressions for α and Γ are given elsewhere.[7] The term ϵ appearing in Eq. (3) is rather poorly understood,[8] but it is ordinarily fairly close to unity and is only important in the anomalous transmission case.

TABLE I. Experimental and theoretical values of the x-ray scattering factors for silicon and germanium. The errors represent an assessment of the total error in the measurement. Statistical errors are much smaller.

Reflection	$\sin\theta/\lambda$	Theory Hartree-Fock free atom	Wölfel and Göttlicher	Present results
		Silicon ($a_0=5.431$ Å, Debye $\Theta=543$°K).		
111	0.1595	10.62	10.80	10.80±0.08
220	0.2604	8.70	8.68	8.70±0.06
311	0.2911	8.15	8.08	8.07±0.08
222	0.3189	0	0.22	0.18±0.01
400	0.3683	7.64	7.43	7.69±0.08
331	0.4013	7.19	7.44	7.41±0.10
422	0.4117	6.72	6.92	6.83±0.10
333	0.4784	6.50	{6.52}	6.50±0.08
511	0.4784	6.50		6.56±0.09
440	0.5207	6.05	6.05	6.05±0.08
444	0.6379	4.99	5.00	5.10±0.08
660	0.7811	3.86		3.76±0.07
555	0.7973	3.78	{3.64}	3.64±0.07
751	0.7973	3.78		3.64±0.07
666	0.9568	0		<0.05
880	1.041	2.54		2.31±0.07
777	1.116	2.30		2.28±0.07
888	1.276	1.92		1.90±0.06
10,10,0	1.302	1.86		1.82±0.06
		Germanium ($a_0=5.657$ Å, $\Theta=293$°K)		
111	0.1531	27.50		27.55±0.2
220	0.2500	23.76		23.90±0.2
222	0.3062	0		too weak to observe
400	0.3535	20.95		20.9 ±0.6
333	0.4593	17.50		17.52±0.2
440	0.4999	16.55		16.62±0.15
444	0.6124	13.55		13.50±0.15
555	0.7655	10.40		10.23±0.15
777	1.072	7.38		7.23±0.15
888	1.225	6.68		6.65±0.15
10,10,0	1.250	6.67		6.65±0.15

TABLE II. Valence contribution to scattering factors of silicon.

Reflection	Theory [Eq. (6)]	Present results
111	+0.185	+0.18±0.08
220	~0	0±0.06
311	−0.085	−0.08±0.08
222	−0.185	− or +0.18±0.01
400	−0.01	+0.05±0.06
331	+0.07	+0.22±0.08
422	~0	+0.11±0.08
333	−0.04	+0.00±0.05
440	~0	+0.00±0.05
666	~0	<0.05

Since all crystals showed a small angle of miscut (i.e., the diffracting planes and the crystal surface were not exactly parallel) a small and ofttimes insignificant correction was made by averaging over the azimuthal angle for the Bragg case. The corrections were neglected in the Laue case since they were much smaller than the experimental error. A search for umweganregung revealed it to be negligible ($<\frac{1}{2}\%$ in integrated intensities).

IV. RESULTS

The resultant scattering factors corrected for the real part of the anomalous dispersion (+0.10 for silicon, +0.2 for germanium) are given in Table I and they evidence good agreement with the Hartree-Fock values listed in Table I. We have also included the measured values of silicon taken by Wölfel and Göttlicher[5] on powders and the agreement is rather good although there are some discrepancies outside experimental error. The measured linear absorption coefficients μ were 14.67/cm for silicon and 325.5/cm for germanium.

There has been some success in accounting for the lack of spherical symmetry in the charge density of diamond by employing a valence charge density[9] of the form

$$\rho=\mathfrak{A}(1\pm xyz/r^3)^2R^2\,, \qquad (5)$$

where $\mathfrak{A}$ is the normalization constant and R is the Hartree-Fock radial wave function. This charge density has tetrahedral symmetry with lobes along the body diagonals and it gives rise to a scattering factor for the four valence electrons

$$f=4\left\{\langle j_0\rangle\mp\frac{210ihkl\langle j_3\rangle}{106(h^2+k^2+l^2)^{3/2}}-\left[\frac{21}{11}-\frac{105(h^2k^2+h^2l^2+k^2l^2)}{11(h^2+k^2+l^2)^2}\right]\frac{\langle j_4\rangle}{106}-\left[\frac{5}{11}-\frac{105(h^2k^4+h^2l^4+k^2h^4+k^2l^4+l^2h^4+l^2k^4)}{11(h^2+k^2+l^2)^3}+\frac{840(hkl)^2}{11(h^2+k^2+l^2)^3}\right]\frac{\langle j_6\rangle}{106}\right\}\,, \qquad (6)$$

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[7] J. J. DeMarco and R. J. Weiss, Acta Cryst. (to be published).

[8] H. Wagenfeld, J. Appl. Phys. 63, 2907 (1962).

[9] R. J. Weiss, Phys. Letters, 12, 293 (1964).

where

$$\langle j_n \rangle = \int_0^\infty j_n R^2 dr.$$

In order to observe the asphericity of the valence-electron charge density, one must subtract the core contribution. This core contribution becomes increasingly larger for the series C, Si, and Ge. If one can estimate the core contribution to an error of $\approx 1\%$ by employing Hartree-Fock free-atom scattering factors, then the errors in the core contribution are approximately ± 0.02 for C, ± 0.14 for Si, and ± 0.28 for Ge (electron units). Since the asphericity in the valence-electron charge density contributes ≈ 0.1 to the scattering factor and the experimental values are only accurate to $\approx 1\%$, the possibility of identifying such asphericity is good in diamond, only fair in silicon and very poor in germanium. We have attempted such an analysis for silicon in Table II and we see the agreement is good for the forbidden 222 reflection (since no core subtraction is required) and fair for the 111, 220, 311, 331, 400, and 333 reflections. Tables of $\langle j_0 \rangle$, $\langle j_3 \rangle$, $\langle j_4 \rangle$, and $\langle j_6 \rangle$ for the valence electrons in Si are given in Table III.

TABLE III. Values of $\langle j_0 \rangle$, $\langle j_3 \rangle$, $\langle j_4 \rangle$, and $\langle j_6 \rangle$ per valence electron in silicon calculated from the free-atom Hartree-Fock $3p$ radial wave function.

$\sin\theta/\lambda$ (Å)$^{-1}$	$\langle j_0 \rangle$	$\langle j_3 \rangle$	$\langle j_4 \rangle$	$\langle j_6 \rangle$
0	1.0	0	0	0
0.05	0.875	0.085	0.006	0
0.10	0.600	0.044	0.020	0.002
0.15	0.313	0.114	0.065	0.009
0.20	0.117	0.150	0.107	0.025
0.25	0.017	0.153	0.126	0.052
0.30	−0.028	0.131	0.120	0.072
0.35	−0.032	0.098	0.090	0.081
0.40	−0.028	0.068	0.065	0.077
0.50	−0.003	0.026	0.035	0.054
0.60	−0.001	0.006	0.015	0.029
0.70		−0.001	0.002	0.014
0.80		−0.002	−0.001	0.005
0.90		−0.001	−0.001	0.002

In the case of germanium we obtain good agreement with the Hartree-Fock scattering factors employing a value of $\Theta = 293$°K as determined by Batterman and Chipman.[10] It should be emphasized, though, that the low-angle reflections 111, 220, 333, 440, are fairly insensitive to the choice of Debye characteristic temperature.

V. DISCUSSION

The experimental results for germanium are in very good agreement with theory suggesting that the radial charge density of the 28 core electrons ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$) are essentially unaltered when the atom becomes part of the solid. This can be contrasted with Cu, Cr, and Fe which evidence considerable expansion of the $3d$ charge density.[1,2] Nothing can be said about the four valence electrons in germanium since they contribute so little to the total scattering factor.

For silicon the generally good agreement suggests that the radial charge density in the solid is well represented by a superposition of free-atom radial charge densities. In addition, the data in Table II suggest that the valence electrons are approximately represented by Eq. (5) employing the free-atom radial charge density for the valence electrons. These results for silicon must be contrasted with those for aluminum[1] which clearly show an appreciable expansion in the solid of the $2s^2 2p^6$ core charge density.

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[10] B. W. Batterman and D. R. Chipman, Phys. Rev. **127**, 690 (1962).

[11] B. W. Batterman, Phys. Rev. **127**, 686 (1962).