

Lawrence Berkeley National Laboratory

LBL Publications

Title

ELECTRONIC CHARGE DENSITY OF ALUMINUM

Permalink

<https://escholarship.org/uc/item/48n1d15r>

Author

Walter, John P.

Publication Date

1972-06-01

Submitted to Physical
Review Letters

LBL-893
Preprint

ELECTRONIC CHARGE DENSITY OF ALUMINUM

John P. Walter, C. Y. Fong, and Marvin L. Cohen

June 1972

AEC Contract No. W-7405-eng-48



For Reference

Not to be taken from this room

LBL-893

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

U 5 0 0 3 8 0 1 5 0 4

Electronic Charge Density of Aluminum*

John P. Walter
Department of Physics, Brandeis University,
Waltham, Massachusetts 02154†, and
Department of Physics, University of California,
Berkeley, California 94720

and

C. Y. Fong
Department of Physics, University of California,
Davis, California, 95616‡ and
Department of Physics, University of California,
Berkeley, California 94720

and

Marvin L. Cohen
Department of Physics, University of California,
Berkeley, California 94720, and
Inorganic Materials Research Division, Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720

Abstract

The valence electronic charge density is calculated for aluminum from wavefunctions obtained via Ashcroft's pseudopotential. A contour plot of the charge density is presented in the (100) plane. The Fourier transform of the charge density is used to calculate the atomic form factors which are compared with experimental x-ray form factors. The accuracy of the wavefunctions are further tested by com-

*Supported in part by National Science Foundation Grant GP 13632.

†Present address.

‡Permanent address.

paring calculations of the imaginary part of the frequency dependent dielectric function with and without the effect of core states.

In this letter we present a calculation of the valence electronic charge density for aluminum. The calculation is based on a pseudopotential band structure calculation.¹ Previous calculations of this type have been done only for semiconductors.²

The wavefunctions used in the charge density calculation were also used to compute x-ray form factors. The agreement with experiment is quite good and the results illustrate the role³ of solid-state or crystalline effects. A further check on the validity of the wavefunctions used comes from a computation of the optical constants for aluminum.

The energy bands and wavefunctions are computed using Ashcroft's⁴ pseudopotential for aluminum. The charge density is calculated from the wavefunctions which are expanded in about 85 plane waves and evaluated² on a grid of 3360 points in the Brillouin zone (70 points in 1/48 of the Brillouin zone). Core states were not included. To illustrate the results in detail, the charge density, $\rho(\vec{r})$ is evaluated at over 1600 points in a (100) plane. This plane intersects a face-centered atom and four nearest

neighbors; the extended plane intersects four of the next-nearest neighbors.

The density $\rho(\vec{r})$ is shown in a contour plot in Fig. 1 in units of e/Ω where Ω is the volume of the primitive cell ($\Omega = a^3/4$). Since the sum is over occupied levels, i. e. energies less than the Fermi energy, there are 3 valence electrons per primitive cell, giving an average charge density of 3. The core electrons are excluded and the charge density varies only between 1.7 at the atom to 3.4 in the interstitial region. It is interesting to compare this with the results for covalent crystals like germanium² where the range of variation is $1 \leq \rho(\vec{r}) \leq 27$ with an average value of 8. The relatively small variation for Al is consistent with the expected nearly free electron picture of metals. The charge build-up halfway between nearest neighbors is the result of additive overlap of spherical shells of charge about each atom. These electron shells have larger radii in the crystal than for the free atom case, and this has a significant effect on the atomic form factors of aluminum.

The valence contribution to the atomic form factors is merely the Fourier transform of the valence charge density. This contribution is added to the core-electron contribution to determine the theoretical form factors for the atoms in the crystal. A comparison of the experimental and theoretical form factors appears in Table I.

Several factors complicate a direct comparison of experimental and theoretical form factors for aluminum. The most important factor is the discrepancies in the experimental x-ray measurements. Sirota⁵ describes these discrepancies and the multitude of problems in the x-ray determina-

tion of form factors. Sirota's opinion is that the early x-ray measurements were carefully done and are still valid today. In view of the differing measurements, we have tabulated the results of two experiments in Table I. The work of Batterman, Chipman and DeMarco⁶ is the most recent, but the results of Brindley⁷ fall about in the middle range of all available x-ray measurements on Al.

The theoretical Hartree-Fock atomic and core form factors that appear in Table I are given by Clementi.⁸ The discrepancy in the theoretical form factors calculated by different authors^{3, 8-10} is only about 1 to 2%, significantly smaller than the discrepancy in the experimental measurements. The theoretical atomic form factors in Refs.^{3, 8-10} are for free atoms. Only Arlinghaus³ attempts a calculation for atoms in a crystal, and his result does not differ significantly from the free-atom result.

A study of Table I shows that when our valence contribution is added to the core contribution, the result is in good agreement with the experiment by Brindley,⁷ but does not agree as well with the experiment by Batterman et al.⁶ However, the agreement of our theoretical form factors with either set of experimental results is better than the agreement of the Hartree-Fock form factors with the same experiments. This superior agreement occurs because the valence electrons in our calculation are in a crystalline environment and consequently are less tightly bound to the individual atoms. The shell of valence electrons has a greater radius in the solid and the valence-electron density is smaller at the atomic site than in the free atom. The agreement between the experiment of Brindley⁷ and our

theoretical values appears to be within experimental error.

The possibility exists that the measurements of Batterman et al.,⁶ are the most accurate. However, the form factors for the valence electrons alone cannot account for the large differences between the measurements of Batterman and the theoretical form factors. This would imply that the core electrons are more diffuse in the solid than the Hartree-Fock calculations indicate. But the (2p) core states lie about 70 eV below the Fermi level, and therefore the crystalline environment should not perturb the core states significantly. Thus, there would appear to be an error in the Hartree-Fock wavefunctions if we were to accept the results of Batterman. Because of the large spread in the experimental measurements, we cannot make more definite conclusions on this point at this time.

Another check on our wavefunctions involves the evaluation of the imaginary part of dielectric function, $\epsilon_2(\omega)$. Several authors have compared the calculated magnitude of the peak in $\epsilon_2(\omega)$ at 1.6 eV with experiment^{11-15,18}. We have also concentrated our attention on this peak. We used here the same scheme as described in Ref. 16 to calculate the $\epsilon_2(\omega)$. To be consistent with our calculation of the charge density, we calculate $\epsilon_2(\omega)$ by setting up the energies and dipole moment matrix elements at 46 points in $\frac{1}{48}$ th of the Brillouin zone using control energies^{1,17} $E_1 = 17.1$ and 4.1 in the units of $(2\pi/a)^2$. The former value of E_1 is used in the charge density calculation and the latter value gives a pseudopotential Hamiltonian matrix of the order of 8. We neglect the Löwdin-Brust perturbation¹ because changing E_1 from 4.1 to 17.1 causes the energies to change by about 0.003eV.

The magnitude of $\epsilon_2(\omega)$ at 1.6 eV with $E_1 = 17.1$ is 50.9 and the corresponding one for $E_1 = 4.1$ is 45.4. The difference is about 10%. We therefore expect that we can explore the effect of the core wavefunction on $\epsilon_2(\omega)$ using the $E_1 = 4.1$ to the right order of magnitude.

The effect of the core wavefunctions on the magnitude of the $\epsilon_2(\omega)$ has been studied by the same scheme described in Ref. 16. The results are shown in Fig. 2. The $\epsilon_2(\omega)$ given in Fig. 2 was calculated using $E_1 = 4.1$ with a mesh of 356 points in the Brillouin zone. The change in the magnitude of the 1.6 eV peak in going from 46 to 356 points increases by only 4%. The atomic-like part of the actual wavefunctions is taken into consideration by a linear combination of core states. The coefficient of the linear combination is obtained by orthogonalizing the actual wavefunction to the core states. The effective atomic number, Z_{eff} , for the (2s) and (2p) core states ranges from 4-12. We determine the Z_{eff} by requiring the overlap between the nearest neighbors of the core wavefunction to be less than 1%. In this way, we obtained a Z_{eff} of 9. The $\epsilon_2(\omega)$ with dipole matrix elements calculated from the actual wavefunctions gives 42.2 for the 1.6 eV peak. The change is therefore quite small. This result is consistent with the conclusion on the dipole matrix elements made by Beeferman et al.¹²

In summary we have shown that the Ashcroft pseudopotential which has been used to compute the Fermi surface¹ of Al can also yield accurate wavefunctions. We have shown that these wavefunctions can be used to explicitly calculate the valence electronic charge density, and optical constants.

Acknowledgement

We would like to thank Professor D. Beaglehole for sending us results of his measurements on Al. CYF would like to express his gratitude to Professors C. Kittel and M. L. Cohen for their hospitality during his stay at Berkeley. Part of this work was done under the auspices of the U. S. Atomic Energy Commission.

References

1. M. L. Cohen and V. Heine, Solid State Physics 24 (Academic Press, Inc., New York, N. Y. 1070), p. 37.
2. J. P. Walter and M. L. Cohen, Phys. Rev. Letters 26, 17 (1971); Phys. Rev. B4, 1877 (1971).
3. F. J. Arlinghaus, Phys. Rev. 153, 743 (1967).
4. N. W. Ashcroft, Phil. Mag. 8, 2055 (1963).
5. N. N. Sirota, Acta Cryst. A25, 223 (1969).
6. B. W. Batterman, D. R. Chipman and J. J. DeMarco, Phys. Rev. 122, 68 (1961).
7. G. W. Brindley, Phil. Mag. 21, 778 (1936).
8. E. Clementi, "Tables of Atomic Functions", Suppl. to IBM J. Res. and Dev. 9, 21 (1965).
9. A. J. Freeman, Acta Cryst. 12, 261 (1959); P.A. Doyle and P. S. Turner, Acta Cryst. A24, 390 (1968); D. T. Cromer and J. T. Waber, Acta Cryst. 18, 104 (1965); F. Herman and S. Skillman, Atomic Structure Calculations (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1966).
10. International Tables for X-ray Crystallography, Vol. 3, (Birmingham,

Kynich Press, 1962).

11. A. J. Hughes, D. Jones, and A. H. Lettington, J. Phys. C2, 102 (1969).
12. L. W. Beeferman and H. Ehrenreich, Phys. Rev. B2, 364 (1970).
13. H. Ehrenreich, H. R. Philipp and B. Segall, Phys. Rev. 132, 1918 (1963).
14. G. Dresselhaus, M. S. Dresselhaus and D. Beaglehole, Programme and Abstracts of the Third Materials Research Symposium, Electronic Density of States, Gaithersburg, Md., Nov. 1969, p. 27.
15. D. Brust, Phys. Rev. B2, 818 (1970).
16. C. Y. Fong, M. L. Cohen, R. R. L. Zucca, J. Stokes and Y. R. Shen, Phys. Rev. Letters 25, 1486 (1970).
17. M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966).
18. D. Beaglehole and M. Wihl (to be published).

Table Caption

Table I Comparison of the theoretical and experimental values of atomic form factors for aluminum. The first column lists reciprocal lattice vectors; the second column, the valence form factors calculated by the authors; the third column, the form factors derived from the Hartree-Fock (HF) core wavefunctions ($1s^2, 2s^2, 2p^2$); the fourth column, the form factors from the HF total wavefunctions ($1s^2, 2s^2, 2p^6, 3s^2, 3p^1$); the fifth and sixth columns, experimental x-ray form factors; the seventh column, the sum of the core and valence form factors.

Figure Captions

Fig. 1 Total charge distribution for the occupied states of aluminum in the 100 plane.

Fig. 2 Comparison of theoretical interband $\epsilon_2(\omega)$ around 1.6 eV calculated from pseudowavefunctions and wavefunctions including core effects. The experimental results are also shown for reference.

Table I

\vec{G}	Valence	SCHF Core ^(a)	Total SCHF ^(a)	Experiment ^(b)	Experiment ^(c)	Valence plus one
000	3.000	10.00	13.00	13.00	13.00	13.00
111	-0.056	8.87	8.94	8.63 ± .14	8.83	8.81
200	-0.203	8.53	8.50	8.25 ± .14	8.24	8.33
220	0.013	7.38	7.31	7.09 ± .13	7.23	7.39
311	0.003	6.67	6.65	6.42 ± .12	6.55	6.67
222	0.000	6.45	6.45	6.19 ± .13	6.42	6.45
400	0.002	5.76	5.78	5.48 ± .15	-	5.76

(a) E. Clementi, "Tables of Atomic Functions", Suppl. to IBM Journ. Res. of Dev. 9, 2 (1965).

(b) B. W. Batterman, D. R. Chipman, and J. J. DeMarco, Phys. Rev. 122, 68 (1961).

(c) G. W. Brindley, Phil. Mag. 21, 778 (1936).

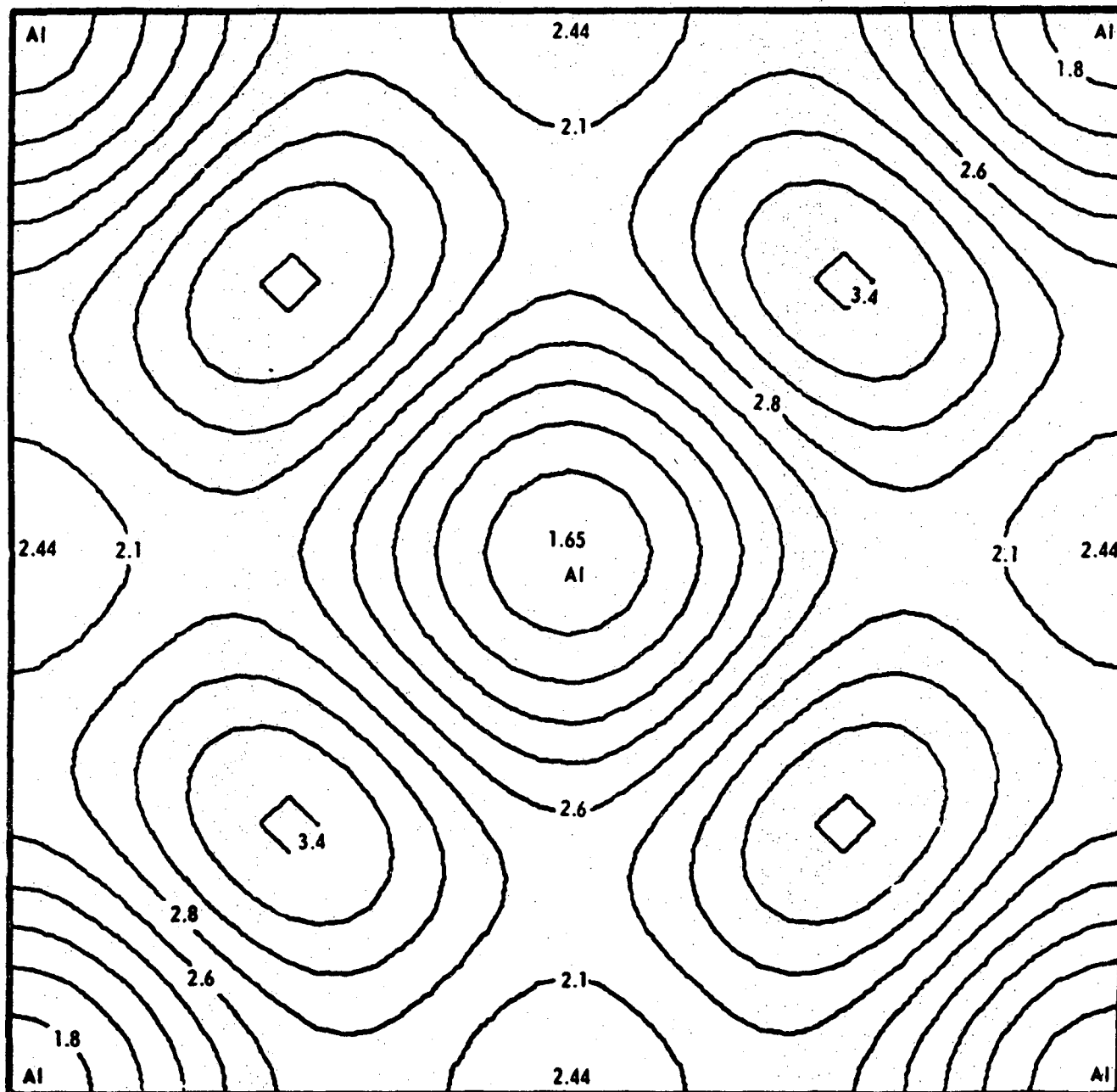


Fig. 1

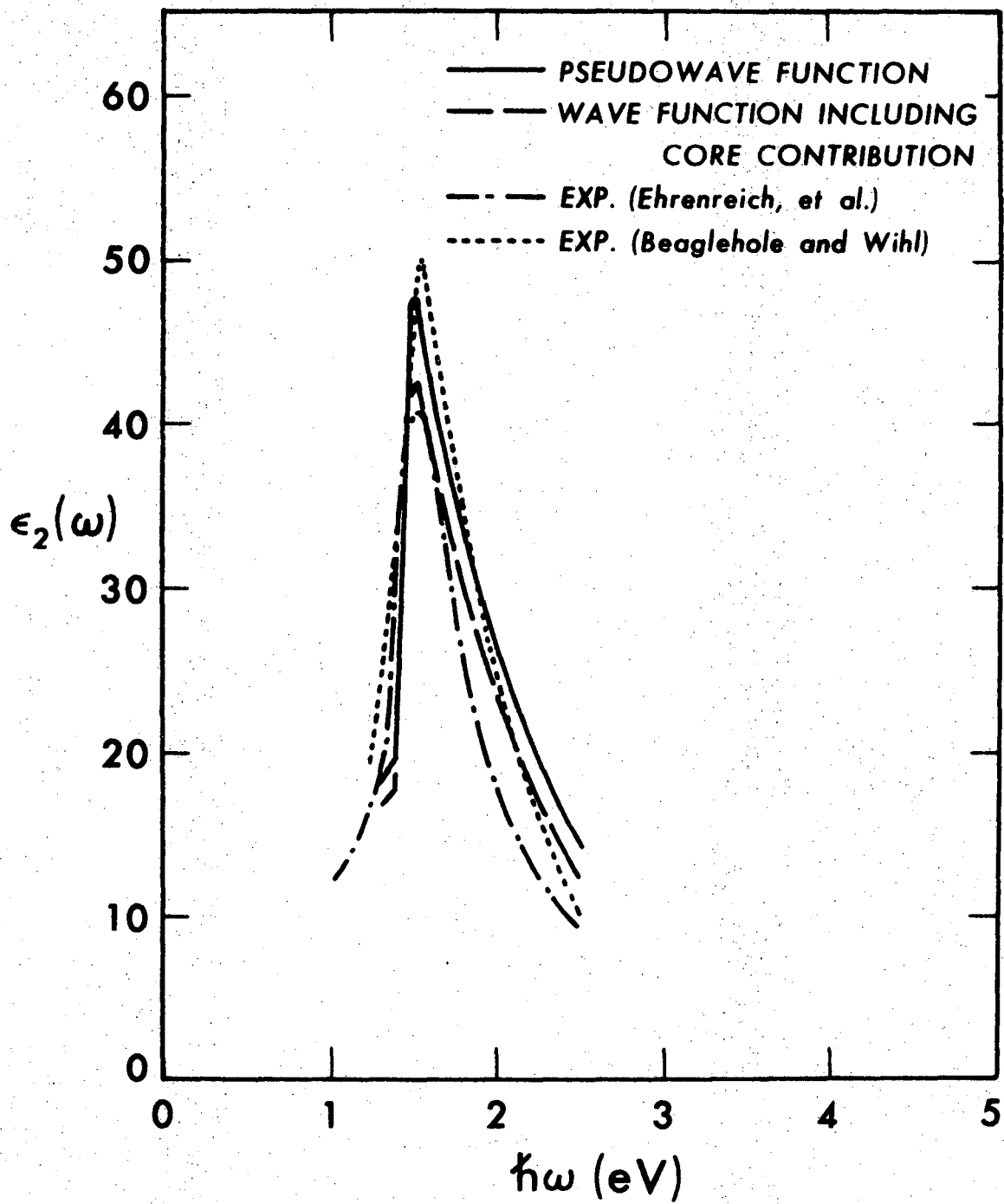


Fig. 2

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720