Bonding in GaAs

J. M. Zuo, J. C. H. Spence, and M. O'Keeffe[(a)]
Department of Physics, Arizona State University, Tempe, Arizona 85287
(Received 22 February 1988)

Experimental measurements of structure factors in GaAs have been compared with the results of *ab initio* calculations by the pseudopotential method. We measure the charge in the bond from charge-density maps to be 0.071 electron, in good agreement with theory. The measurements were obtained by an electron-diffraction technique which can be applied to submicron crystals, thus greatly extending the range of materials for which structure factors can be measured, and theoretical calculations tested.

PACS numbers: 61.14.Dc, 61.16.Di, 71.20.−b

The extremely small magnitude of crystal structure-determining energies compared with their cohesive energy has long provided a severe challenge for theoretical calculations of crystal structure. Small errors in the calculation of the strong Coulomb interactions may easily mask the very weak interactions which stabilize particular crystal structures. Similarly, bonding charge densities in covalent crystals are typically less than 0.01% of the total charge density. The success of the pseudopotential method in the local-density-functional approximation for the calculation of the ground-state properties of single crystals and their surfaces[1] has, however, greatly increased the accuracy with which valence electron densities may be computed.

These advances in theory have not been matched by advances in the accuracy of experimental methods for the determination of charge-density distributions in materials. For the special case of silicon (for which very large defect-free crystals can be grown), accurate determinations have been made with use of the x-ray *Pendellosung* method; however, an urgent need exists for a method which can be applied to submicron structures and polycrystalline materials for comparison with band-structure calculations. In this Letter we therefore describe a versatile and accurate general method for the experimental measurement of structure-factor amplitudes from microcrystals of known structure, and compare our results for the bonding charge in GaAs with the results of recent pseudopotential calculations. The method is based on a quantitative comparison of energy-filtered transmission electron microdiffraction patterns ("rocking curves") with multiple-scattering calculations. The low-order Fourier coefficients of the crystal potential are adjusted for best fit with the experimental data. Unlike spectroscopic techniques, our method ensures (through energy filtering for elastic scattering) that only ground-state (and phonon excitation) effects are observed. The enhanced sensitivity to bonding effects of low-order electron diffracted beams over the corresponding x-ray reflections results[2] from the Mott-Bethe relationship between the x-ray scattering factor $f_x(s)$ and the electron scattering factor $f_e(s)$ for an atom of atomic number Z:

$$f_e(s)=\frac{me^2}{2h^2}\frac{Z-f_x(s)}{s^2}, \quad (1)$$

where $s=(\sin\vartheta)/\lambda$ (m,λ relativistically corrected). Equation (1) expresses Poisson's equation in the Fourier domain. Thus, for small ϑ, small changes in the Fourier coefficients of charge density, $f_x(s)$, have a large effect on $f_e(s)$, the coefficients of potential. This sensitivity is further enhanced by strong multiple scattering which normally occurs in electron diffraction.

Attempts to develop a quantitative method of electron crystallography have a long history.[3,4] For particular specialized cases, the critical voltage method can provide a highly accurate method for certain structure factors.[5] Two- and three-beam approximations[6,7] have also proved useful. The important problems have always been the size of the computational effort needed to include all multiple-scattering effects, the avoidance of crystal defects, the accurate determination of experimental parameters, and the accurate specification of Debye-Waller factors (needed for comparison of results at different temperatures). Advances in computers have solved the first problem for simple structures, Advances in instrumentation for convergent-beam electron diffraction (CBED), such as brighter sources, efficient energy-loss spectrometers, and improved vacuum systems allowing nanometer-sized electron probes without contamination, have solved the second. Our experimental parameters are treated as refinement parameters on an equal footing with the structure factors sought. Figure 1 shows how rocking curves are obtained simultaneously in every diffracted order by the CBED method. Thus many of the difficulties of the x-ray method (extinction, crystal defects, and dispersion corrections) are avoided, and greater sensitivity obtained for low-order reflections. (Extinction effects in x-ray refinement causes the biggest error for the crucial low-order reflections.)

Our calculations for the CBED intensities are based on the Bloch-wave solutions for the Schrödinger equation due to Bethe,[8] given, for example, in Ref. 8. To obtain greater accuracy we solve the fully three-dimensional

© 1988 The American Physical Society

diffraction problem (thereby including all higher-order Laue zone reflections) by the renormalized eigenvector method.[9] For a parallel-sided slab of crystal traversed by an electron beam inclined to the surface normal $\hat{\mathbf{n}}$ we obtain

$$\frac{B_{\mathbf{g}}(2\mathbf{k}\cdot\mathbf{g}+\mathbf{g}^2)}{1+g_n/K_n}-\sum_{\mathbf{h}}\frac{B_{\mathbf{h}}U_{\mathbf{g}-\mathbf{h}}}{(1+g_n/K_n)^{1/2}(1+h_n/K_n)^{1/2}}=-2K_n\gamma B_{\mathbf{g}}, \tag{2}$$

for eigenvalues γ, eigenvectors $B_g=(1+g_n/K_n)^{1/2}C_g$ (see Ref. 8 for definition of C_g), complex "structure factors" U_g (see Ref. 8), electron wave vector $\mathbf{K}$, and reciprocal-lattice vectors $\mathbf{g}$. Here $g_n=\mathbf{g}\cdot\hat{\mathbf{n}}$, $K_n=\mathbf{K}\cdot\hat{\mathbf{n}}$, and the wave vector inside the crystal is $\mathbf{k}=\mathbf{K}+\gamma\hat{\mathbf{n}}$. We solved these equations numerically to obtain the CBED intensity at a point (K_x,K_y) in the CBED pattern,

$$\mathbf{I}_{\mathbf{g}}(K_x,K_y)=\sum_i\sum_j C_0^i(\mathrm{inv})C_{\mathbf{g}}^iC_0^j(\mathrm{inv})^*C_{\mathbf{g}}^{j*}\exp[-2\pi i(\gamma^i-\gamma^j)t], \tag{3}$$

where C_g^i and γ^i functions of K_x and K_y. Here $C_0^i(\mathrm{inv})$ are the elements of the first column of the inverse of the matrix whose elements are C_g^i (rows i, columns g). Effects of inelastic scattering ("absorption") have been included through the addition of a small imaginary component[8] to U_g. The resulting non-Hermitean eigenvalue problem was solved by standard numerical methods. High-order structure factors (insensitive to bonding) were taken from relativistic Hartree-Fock calculations for neutral atoms.[10] A matrix diagonalization is required for each plane-wave component of the incident cone of electrons. The dimension 50×50 was required to include all reflections near the Ewald sphere which gave appreciable intensity, and to ensure convergence. The refinement parameters (high voltage, sample thickness, absorption parameters, selected structure factors) were varied as described below for best fit. Debye-Waller factors for 90 K were taken from recent lattice-dynamical calculations,[11] which agree to within 10% with neutron-diffraction data. (An error of 20%, however, would account for only one-third of the difference between our experimental and neutral-atom results.)

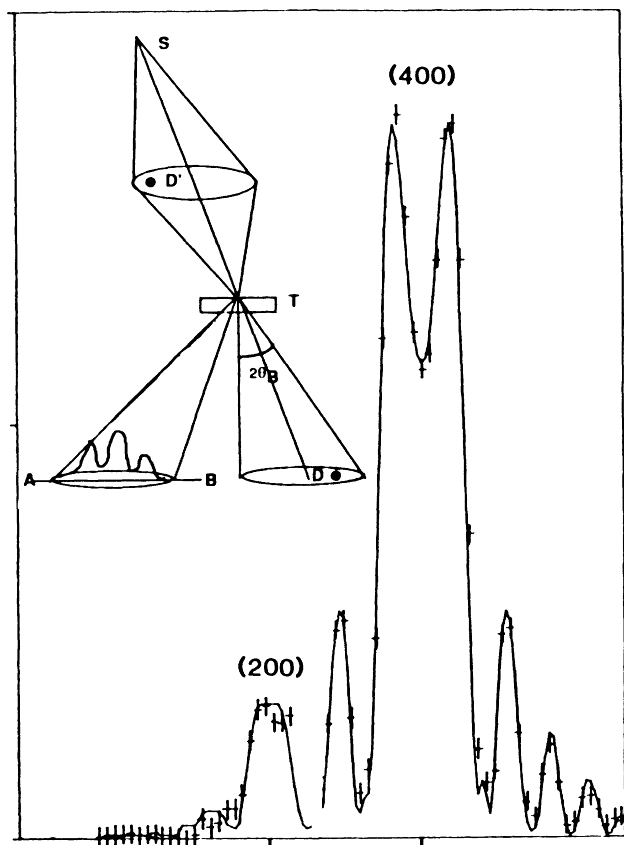

FIG. 1. Experimental data (crosses) for the (h00) systematics, compared with three-dimensional dynamical theory (continuous line). Beam direction [035]; 120 kV; −183 °C; elastic scattering only. Thickness, 88 nm. (200) and (400) Bragg conditions indicated. Inset: Ray diagram for CBED. S, electron source; D, detector; D′ is conjugate to D; θ_B, the Bragg angle; T, the sample. Scans are taken across A-B.

GaAs was prepared for electron microscopy by grinding and ion milling at 90 K. CBED patterns were obtained with use of a Philips model-EM400 electron microscope from defect-free regions (confirmed by imaging) at an accelerating voltage of 120 kV and 90 K (to minimize phonon scattering and reduce contamination). By our placing the deflection of the CBED pattern under computer control, the intensity variation along a "systematics" line could be scanned over the entrance slit of an energy-loss spectrometer (Gatan model 607). Angular resolution was 0.6% of the (200) Bragg angle. Electron-beam stability was assured by our comparing intensities before and after scans. Intensity data along the entire systematics line with reflection g at the Bragg condition were used to refine U_g, and this procedure was repeated for each g. Our refinement strategy emphasized the portion of the data most sensitive to each parameter as follows: (1) High voltage and orientation were found from the positions of higher-order Laue zone lines; (2) absorption parameters were determined by our matching the asymmetry of the central disk; (3) thickness was found with use of the outer fringes of the CBED disks; (4) structure factors were refined with use of the whole curve, stressing the inner CBED peaks at the Bragg condition. Thicknesses $t=(n+\frac{1}{4})\xi_g$ give greatest sensitivity to U_g and t. The phonon-scattering background included in our 2-eV elastic window was measured at 90 K between the disks to be 1% of the

Bragg intensity, and was subtracted. The much larger plasmon and electronic contribution is excluded by the filter. Figure 1 shows results after refinement. Table I summarizes these and compares them with the recent one-electron local-density-functional–approximation pseudopotential calculations of Nielsen and Martin,[12] to which a core contribution has been added.[12] In GaAs, only those structure factors whose indices h,k,l are odd have phases affected by charge redistribution (others have known phases $n\pi$). X-ray results are also shown,[13] corrected for dispersion and Debye-Waller factors.[12] The (200) and (000) [14] structure factors cannot easily be measured by x-ray methods.

Our results are consistently 1 to 2 e^-/cell larger than the crystal theory results.[12] Since a similar difference is likely to result from a measurement of the imaginary parts of the odd reflections, their phase can be well approximated by calculated phases.[12] It is well known[15] that, in the presence of multiple scattering, both x-ray and electron-diffraction intensities are sensitive to structure-factor phases. Our systematics geometry is not highly sensitive to the small changes in the phases of the odd reflections due to bonding, because it tends to be dominated by two-beam interactions which do not preserve phase information. However, it is readily shown that the important charge density near the midbond is almost independent of these phases, which mainly affect charge transfer between the large "hole" in Fig. 2 and the nuclear positions. (The greatest uncertainty in the pseudopotential results[12] also lies at the nucleus.) Because of the very small relative size of bonding charges, valence charge-density maps are almost indistinguishable from maps formed from a superposition of neutral atoms on lattice sites. They thus contain no useful information on crystal bonding. As a more sensitive method of showing our results, Fig. 2 shows a charge-density difference map $\Delta\rho(r)=\rho_e(r)-\rho_a(r)$ on the (1,−1,0) plane containing the interatomic bond. Here $\rho_e(r)$ was found from the measured U_g, with use of Eq. (1). Since $\rho_a(r)$ was found from the same neutral-atom scattering factors[10] used in the dynamical calculations, Fig. 2 depends only on measured quantities [together with the calculated phases for the (111) and (333) reflections]. Results of a complete error analysis[16] are given in Table I. For Si it has been found[4] that the CBED and x-ray method (Aldred and Hart[17]) agree to within 0.3%, giving confidence in the method. Unlike this earlier work, we have used energy-filtered patterns and three-dimensional dynamical calculations which allow for inclined boundary conditions, and therefore expect more accurate results.

Figure 3 shows the bonding charge $\Delta\rho(r)$ along the interatomic Ga−As bond. GaAs is partially ionic and does not have a center of symmetry at the midbond position. Thus in Figs. 2 and 3 we see a reduced covalent bond peak (increased negative charge) on the As side of the midbond position. The negative value of $\Delta\rho$ around Ga may be accounted for by a dilation of that atom, and corresponding contraction of the As. We also find that more negative charge surrounds the As atom than the Ga. A similar study of more ionic semiconductors might be expected to continue this trend. The total amount of charge in the bond, defined as the sum of all positive $\Delta\rho$ in a cube on (1,−1,0) whose body diagonal is the bond, is 0.071 ± 0.045 electron. This may be compared with the theoretical value[1] of 0.08 electron, showing excellent agreement, given the arbitrariness in the definition of the background charge and bond volume. The development of this method thus opens the way to the accurate determination of charge densities in a wide range of real ma-

TABLE I. Structure factors in GaAs (in electrons per unit cell). (a) Experimental results from the present CBED study, compared with (b) pseudopotential calculations (Ref. 12), (c) x-ray results (Ref. 13), and (d) neutral-atom calculations (Ref. 10). Debye-Waller factors have been removed from all results (Ref. 11). Total crystal potential values V_g are also given.

hkl	CBED	Theory	X ray	Atoms	V_g (V)
000	···	···	···	···	13.2 ± 0.6
111	156.3 ± 0.3	155	157.6 ± 0.4	155.1	6.65 ± 0.07
200	5.86 ± 0.04	5.92	···	5.58	0.43 ± 0.008
220	189.4 ± 0.4	187.8	189.2 ± 0.4	190.2	6.63 ± 0.04
400	162.9 ± 0.6	160.4	165.2 ± 0.5	163.3	4.57 ± 0.05
333	97.3 ± 0.8	96.0	99.6 ± 0.3	97.8	2.39 ± 0.02

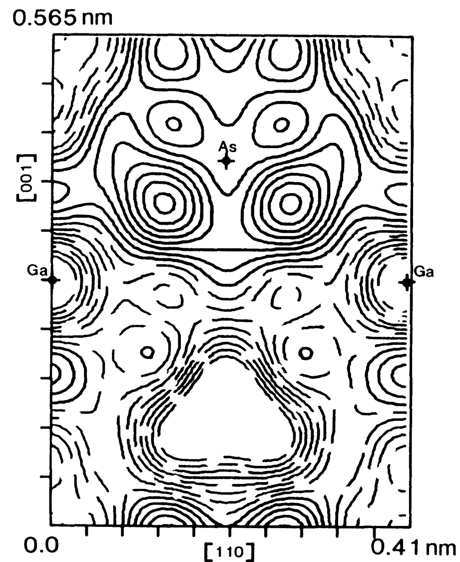

FIG. 2. Charge-density difference map $\Delta\rho(r)$ for GaAs on the (1,−1,0) plane containing the interatomic bond. Continuous lines, electron surplus regions (with respect to "neutral atoms"); dashed lines, electron-deficient regions. Contour increment 0.011 electron per cubic angstrom.

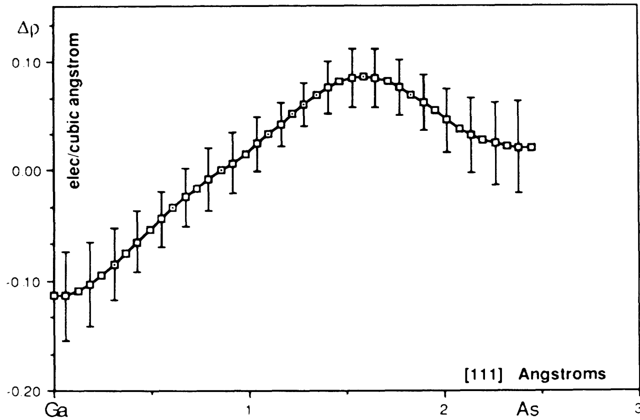

FIG. 3. Charge-density difference along the interatomic Ga—As bond. Ionic and covalent effects are both evident.

terials.

We are grateful to Professor J. Gjonnes, Professor R. Hoier, Professor P. Rez, and Professor J. Northrup, and to K. Gjonnes for discussions. This work was supported by National Science Foundation Grants No. DMR8741208 and No. DMR8418083, and the National Science Foundation-Arizona State University National Center for Electron Microscopy.

[a]Department of Chemistry.

[1]See articles by M. Cohen, by A. Zunger, and by others, in *Structure and Bonding in Crystals,* edited by M. O'Keeffe and A. Navrotsky (Academic, New York, 1981).

[2]J. M. Cowley, Acta Crystallogr. **6**, 516 (1953).

[3]C. H. MacGillavary, Physica (Utrecht) **7**, 329 (1940); D. J. Smart and C. J. Humphreys, in *Electron Diffraction 1927–1977,* edited by P. J. Dobson *et al.*, IOP Conference Proceedings No. 41 (Institute of Physics, Bristol and London, 1978), p. 145; P. Goodman, Acta Crystallogr., Sect. A **32**, 7932 (1976); R. Vincent, D. M. Bird, and J. W. Steeds, Philos. Mag. A **50**, 765 (1984); T. Shishido and N. Tanaka, Phys. Status Solidi (a) **383**, 453 (1976).

[4]R. Voss, G. Lehmpfuhl, and J. Smith, Z. Naturforsch. **59**, 973 (1980).

[5]J. R. Sellar, D. Imeson, and C. J. Humphreys, Acta Crystallogr., Sect. A **36**, 686 (1980).

[6]K. Gjonnes, J. Gjonnes, J. Zuo, and J. C. H. Spence, Acta Crystallogr. (to be published).

[7]J. Tafto and J. Gjonnes, Ultramicroscopy **17**, 329 (1985).

[8]For a review, see C. J. Humphreys, Rep. Prog. Phys. **42**, 1825 (1979).

[9]A. L. Lewis, R. E. Villagrana, and A. J. F. Metherall, Acta Crystallogr., Sect. A **34**, 138 (1978).

[10]*International Tables for X-Ray Crystallography,* edited by J. A. Ibers and W. C. Hamilton (Kynoch, Birmingham, 1974), Vol. 4, Tables 2.2A and 2.4.6A.

[11]J. S. Reid, Acta Crystallogr., Sect. A **39**, 1 (1983).

[12]O. H. Nielson and R. M. Martin, Phys. Rev. B **32**, 3792 (1985).

[13]T. Matsushita and J. Hayashi, Phys. Status Solidi (a) **41**, 139 (1977).

[14]N. Yamamoto and J. C. H. Spence, Thin Solid Films **104**, 43 (1983).

[15]For x rays, S. Chang, Cryst. Rev. **1**, 87 (1987). For electrons, K. Kambe, J. Phys. Soc. Jpn. **12**, 1 (1957); J. Gjonnes and R. Hoier, Acta Crystallogr., Sect. A **27**, 313 (1971); D. Bird, R. James, and A. R. Preston, Phys. Rev. Lett. **59**, 1216 (1987).

[16]J. M. Zuo, M. O'Keeffe, and J. C. H. Spence, in Proceedings of the Electron Microscopy Society of America, edited by G. Bailey (San Francisco Press, San Francisco, to be published).

[17]P. J. E. Aldred and M. Hart, Proc. Roy. Soc. London A **332**, 223 (1973).