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First-principles calculation of the dielectric properties of GaAs: Dielectric constant, effective charges, and piezoelectric constant

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We present the results of an *ab initio* calculation of the macroscopic dielectric properties of GaAs. The electronic dielectric constant, the effective charges, and the piezoelectric constant are calculated at several finite wave vectors in the density-functional approach, and these results are extrapolated to zero wave vector. The extrapolated values for the dielectric constant and the effective charges are in excellent agreement with experiment: $\epsilon_\infty = 10.9$ (experiment, 10.9), and $|e_T^*| = 2.32$ (2.16). The extrapolated value of the piezoelectric constant also is in good agreement $(a_0/e^2)e_{14} = -0.14$ (-0.16), although the uncertainty is large.

Although many properties of a crystal can now be calculated from first principles using the density-functional method, those properties involving the long-range part of the Coulombic field are not so easily obtained. The reason for this is that quantities such as the electronic dielectric constant, the optic-mode effective charges, and the piezoelectric constant are defined by taking a small wave-vector limit. In the density-functional approach the small wave-vector limit means calculating with supercells which become infinite in size, a clearly impossible task. Yet the density-functional method is by far the easiest theoretical tool available which allows one to calculate these properties from first principles. The essential difficulty is to find a way to take the limit correctly to obtain those quantities which measure the response to Coulombic fields.

To the present, there have been several techniques which have been applied to calculating these small wave-vector responses. Two similar calculations[1,2] have obtained results for the electronic dielectric constant and the effective charges. These calculations have used a finite-sized cell to calculate the response to various perturbations. The approximate macroscopic response is obtained by averaging the local electric field over a small region of the supercell to obtain an approximation to the macroscopic field. The difficulty with this approach is to show that the average electric field obtained with the finite-sized cell is close to the true macroscopic one—i.e., that the average electric field does not change as the supercell size changes. Another approach is to use perturbation theory.[3] With perturbation theory, it is possible to take the short wave-vector limit analytically. However, the results are of questionable accuracy, due to the use of the local density approximation to the exchange-correlation potential. None of these approaches has been used to calculate the piezoelectric constant.

In this paper we present the results of calculations of the electronic dielectric constant, the effective charges, and the first *ab initio* calculation of the piezoelectric constant of GaAs. We calculate these quantities at several finite wave vectors, and then extrapolate to the limit of zero wave vector. This method, though less elegant and more costly in terms of computation time than other techniques, suffers from fewer computational and theoretical uncertainties. In addition, calculation of the piezoelectric constant is possible.

We choose our wave vectors to be in the $[11\bar{1}]$ direction, with magnitudes such that the supercells in the density-functional calculation are N times larger than the normal unit cell of GaAs, i.e., $q = 1/N\ (1,1,-1)$ in units of $2\pi/a_0$. We present results of the calculations for $N = 2$, 4, 6, and 8. The magnitudes of these values of q are the smallest that can be obtained using supercells of these sizes, and the direction is chosen to maximize symmetry while still allowing the calculation of the piezoelectric constant. The supercells contain $2N$ atoms.

The electronic dielectric constant is obtained by applying a weak external potential of wave vector q and calculating the self-consistent charge density with the usual techniques of the density-functional method. The dielectric constant is simply the ratio of the external perturbation to the total electrostatic potential:

$$\epsilon_\infty(q)^{-1} = 1 - \frac{4\pi}{q^2}\frac{\rho(q)}{V_{\text{pert}}} \quad . \tag{1}$$

Note that since the charge density is of order q^2, we can expand the real part of the dielectric constant near $q = 0$ in a simple power series in q^2. We do the extrapolation by fitting the results to this power series to obtain a functional form of ϵ_∞ valid near $q = 0$.

The effective charges and piezoelectric constant are somewhat more complicated. In Refs. 4 and 5, Martin and coworker showed that the piezoelectric constant and the dynamic effective charges can be obtained from the dipole and quadrupole moments of the change in charge density induced by the displacement of individual atoms. One can extract these moments from a density-functional calculation as follows. Consider a longitudinal "phonon," in which from each unit cell only the atom located at R^A in the unit cell is displaced, e.g., the Ga atoms in GaAs. Then, the total induced charge density at wave vector q can be obtained from the charge density induced by the displacement of a single atom:

$$\rho(q) = e^{-iq\cdot R^A} \int e^{-iq\cdot r} F_\gamma^A(r)\, u_\gamma\, d^3r \quad . \tag{2}$$

Here, F^A is the charge density induced by the displacement of a single atom, u_γ is the displacement vector of the phonon, and q is the wave vector of the phonon. (We adopt the convention that repeated Greek indices are to be summed.) Taking the limit of small q, we obtain the connection between the total induced charge density and the dipole and quadrupole moments of F^A:

$$\begin{aligned} e^{iq\cdot R^A}\rho(q) &= (-iq_\alpha)\int r_\alpha F^A_\gamma(r)\,u_\gamma\,d^3r \\ &\quad +(-iq_\alpha)(-iq_\beta)\int r_\alpha r_\beta F^A_\gamma(r)\,u_\gamma\,d^3r \\ &= -(iq_\alpha)(e_L^*)_{\alpha\gamma}u_\gamma \\ &\quad +(iq_\alpha)(iq_\beta)(Q_L)_{\alpha\beta\gamma}u_\gamma \ . \end{aligned} \tag{3}$$

Note that if we could calculate $\rho(q)$ for small enough q, we could read off directly the moments of F^A, and hence the longitudinal effective charge, from the real and imaginary parts of the charge density. However, as we shall see, calculating with a q small enough implies supercells so large that computation becomes impractical.

We define q-dependent moments as follows. We choose u to be parallel to q, so that the phonon is longitudinal, i.e., $u=a_0\delta/2\ (1,1,-1)$. Plugging q and u into Eq. (3) and using the symmetry of the GaAs, we find that a q-dependent longitudinal effective charge and quadrupole moment can be written

$$\begin{aligned} e_L^* &= -\frac{N\Omega_0}{3\pi\delta}\,\mathrm{Im}[e^{iq\cdot R}\rho(q)] \ , \\ Q^L_{xyz} &= \frac{a_0\Omega_0N^2}{6\pi^2\delta}\,\mathrm{Re}[e^{iq\cdot R}\rho(q)] \ . \end{aligned} \tag{4}$$

As was the case with the dielectric constant, the q-dependent moments are smooth functions near $q=0$. We can obtain the macroscopic limit by calculating these moments at various N, and then fitting the results to a simple polynomial in powers of q^2 (equivalently, powers of $1/N^2$).

In the actual density-functional calculations, we use the local ionic pseudopotentials for Ga and As that others have used,[6] and use the local density functional for the exchange-correlation potential, $V_{\mathrm{ex}}(r)=0.8\frac{3}{2}[3n(r)/\pi]^{1/3}$. Other local approximations of the exchange-correlation potential appeared to make little or no difference. The calculation was carried out for supercells of size 2, 4, 6, and 8 times the normal unit cell. In each case, approximately $339\times N$ wave vectors were used. The wave functions were found using a method similar to that of Bendt and Zunger[7] (Lowdin perturbation was not used), and the number of special points used was two for $N=6$ and 8, and four for $N=2$ and 4. For the dielectric constant the magnitude of the perturbing potential was 10^{-3} a.u., which was found to be well within the linear-response region. Similarly, the magnitude of the displacements, $\delta=0.005$, was also found to give a linear response. Up to ten iterations were needed to make sure that the charge density was sufficiently converged.

The results of the calculations are shown in Table I, along with the results of the extrapolation and experimental values. The extrapolation was done by fitting the results for $N=4$, 6, and 8 to a simple polynomial of order 2 in $1/N^2$, $\epsilon_\infty^{-1}(0)+b/N^2+c/N^4$. The results for $N=2$ were not used in the extrapolation, since the results indicated that $N=2$ was not sufficiently close to $q=0$ for the simple power-series expansion around $q=0$ to be valid.

The extrapolation of the results for the dielectric constant agrees with the experimental result with an error of less than 1%, 10.9 in both cases. (We have used ϵ_∞^{-1} as the function to be extrapolated, since ϵ_∞^{-1} is a smooth function of q^2 near $q=0$.) Note that even at the largest N, the error in the value of ϵ_∞^{-1} calculated at that N, is more than 5%. This indicates that the extrapolation is needed for accurate results. Kunc and Resta[1] obtain a dielectric constant between 13.6 and 11.9 with the uncertainty due to the finite size of the supercell. (They used a supercell 8 times larger than the normal unit cell—equivalent to our $N=8$.)

The results for the longitudinal effective charge are almost as good, differing from the experimental results by less than 8%. Noteworthy, however, is the fact that the extrapolated values of the effective charges satisfy the acoustic sum rule[8] (the sum of the effective charges must be zero) to within 1%, in spite of the fact that even at the largest N the sum rule is clearly *not* satisfied. Again, this indicates the need for the extrapolation. As expected, our results give the Ga effective charge as positive. (The sign of the effective charge cannot be determined from experiment.) The transverse effective charge is simply obtained by multiplying the longitudinal effective charge by the electronic dielectric constant, and our result is 2.32, compared to the experimental 2.16. This result is essentially the same as Kunc and Resta's result of 2.27.[1] Our result differs somewhat from the result obtained by Kunc and Martin[2] for the longitudinal effective charge, 0.166. We believe that the latter result was incorrectly calculated, as the electric field was apparently obtained from the self-consistent potential, which includes not only the electrostatic terms, but also the exchange-correlation terms, which do not contribute to the

TABLE I. Results of density-functional calculations at finite wave vectors and the extrapolation to $q=0$ using a polynomial fit, and experimental results. Question marks indicate experimental results not known. (The sign of the effective charges is not known.)

		Ga		As	
N	ϵ_∞^{-1}	e_L^*	Q_L	e_L^*	Q_L
2	0.3103	−0.912	1.82	−2.89	−0.882
4	0.1530	0.474	1.41	0.136	−0.548
6	0.1059	0.296	1.44	−0.0215	−0.766
8	0.0971	0.253	1.47	−0.0986	−0.747
∞	0.0917	0.213	1.55	−0.214	−0.649
Expt.	0.0916	?0.197	?	?0.197	?

electric field. These terms vanish in the long-wavelength limit, but contribute roughly 30% of the total potential for the cell size considered in Ref. 2.

The longitudinal quadrupole moment is also listed in Table I. While the individual quadrupole moments cannot be determined from experiment, the sum of the quadrupole moments does contribute to the piezoelectric constant. From Ref. 4 the piezoelectric constant is given by

$$\left(\frac{a_0}{e^2}\right)e_{14}=\epsilon_\infty\left(\zeta e_L^*-\frac{2}{a_0}(Q_L^{\mathrm{Ga}}+Q_L^{\mathrm{As}})\right) , \tag{5}$$

where ζ is the internal strain parameter. Using our values for e_L^* and Q_L, together with the recent first-principles calculation[9] of ζ, we obtain -0.14 for $(a_0/e^2)e_{14}$, compared to -0.16 from experiment. This apparently excellent agreement is deceiving, because the piezoelectric constant has two large and opposite contributions, and the theoretical value of the internal strain parameter is not very certain.

There are two conclusions to be drawn from this work. First, one now has a method of calculating from first principles the piezoelectric constant, as well as the electronic dielectric constant and the effective charges. Nowhere in this work have we used any parameters beyond the local ionic pseudopotentials.

Secondly, we have demonstrated that long-wavelength limits are not reached with q vectors at which the density-functional method is feasible. For example, to calculate the effective charges without extrapolation, while satisfying the acoustic sum rule to only 10%, requires N to be ~ 22. The computer resources needed for such a calculation are orders of magnitude greater than those required for this paper. Thus the extrapolation saves a tremendous amount of computer time.

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