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COMMENTS AND ADDENDA

Temperature Dependence of the Energy Gap in GaAs

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We show that a recent psuedopotential calculation overestimates the temperature dependence of the band gap in GaAs. We also calculate the individual contributions of the pseudopotential coefficients to the shift with temperature and find that the theoretical shift is dominated by V_{11}^{s}. Hence the disagreement between theory and experiment may result from the arbitrary truncation of the pseudopotential for $G^2 > 11$.

In a recent Letter, Walter, Zucca, Cohen, and Shen[1] have calculated the temperature dependence of the band structure of GaAs using the empirical pseudopotential method, but adequate experimental data were not available to critically evaluate the predicted temperature dependence of the fundamental direct gap. Recent photoreflectance data[2] obtained on ultrapure epitaxial layers of GaAs permit an accurate determination of the energy gap as a function of temperature. We find that the pseudopotential calculation overestimates the decrease in the band gap as the temperature is raised from 0 to 300 °K. In order to locate the physical origin of this discrepancy we have calculated the individual theoretical shifts from the six independent pseudopotential coefficients. We find that almost the entire temperature dependence is due to V_{11}^{s}, the Fourier coefficient of the symmetric part of the pseudopotential for reciprocal-lattice vectors of squared magnitude 11. Since all pseudopotential coefficients for $G^2 > 11$ are constrained equal to zero, we conclude that the disagreement between theory and experiment may result from the arbitrary truncation of the pseudopotential.

The room-temperature energy gap calculated by Walter *et al.*[1] is 1.36 eV, 60 meV below the experimental energy gap from photoreflectance measurements. If this difference between theory and experiment were independent of temperature, it might be corrected by a slight adjustment of the pseudopotential coefficients. Such is not the case as can be seen in Fig. 1 where we compare the theoretical[1] and experimental[2-4] energy gaps for various temperatures.

In a pseudopotential calculation, the temperature dependence of the energy band structure arises

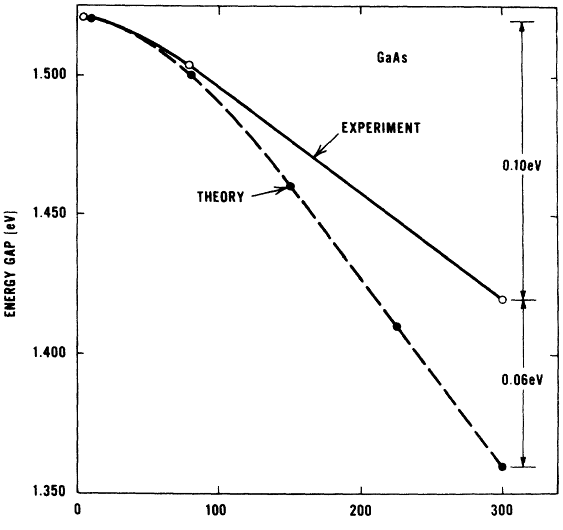

FIG. 1. Comparison of theoretical (Ref. 1) and experimental (Refs. 2 and 3) temperature dependences of the band gap in GaAs.

TABLE I. Debye-Waller screening of the GaAs pseudopotential at 300 °K.

Coefficient	V^{a} (Ry)	$(e^{-W}-1)^{b}$	$\Delta E_g/\Delta V$ (eV/Ry)	ΔE_g (meV)
V_3^s	−0.2460	−0.0132	1.6	5
V_8^s	−0.0008	−0.0352	45.6	1
V_{11}^s	+0.0737	−0.0484	50.8	−181
V_3^A	+0.0583	−0.0132	10.8	−3
V_4^A	+0.0509	−0.0176	3.3	−3
V_{11}^A	+0.0011	−0.0484	−19.2	1
		$E_g(300°) - E_g(0°) = -185$ meV		

[a] Reference 1.

[b] We have used $W/G^2 = 0.0044$ as in Ref. 1.

from two effects[1,5]: (i) an increase in lattice constant as temperature increases, and (ii) Debye-Waller screening of the effective potential. Since the increase in lattice constant contributed only 13% of the total theoretical shift in GaAs,[1] the Debye-Waller screening dominates the disagreement between theory and experiment. In order to ascertain the origin of the discrepancy, we have estimated the contributions of the individual pseudopotential coefficients to the total shift due to screening. The results of this calculation are shown in Table I, where the individual contributions to the shift of the energy gap are approximated by

$$\Delta E_g = (\Delta E_g/\Delta V)\, V(e^{-W}-1). \qquad (1)$$

We have calculated the linear shifts of the energy gap for a unit change in V, i.e., $\Delta E_g/\Delta V$, by repeating the pseudopotential calculation six times, each time changing one of pseudopotential coefficients a small amount,[6] 0.005 Ry. The potentials V are those given by Walter *et al.*[1] at low temperature, and we have used $W/G^2 = 0.0044$ as calculated by Walter *et al.*[1] at 300 °K. The total shift of −0.18 eV calculated in this way compares favorably with the exact value of −0.16 eV and has the advantage that it shows clearly the origin of the temperature dependence.

The striking feature of Table I is that the dominant contribution to the theoretical shift of the energy gap comes from the coefficient V_{11}^s. This same result was also obtained using the original pseudopotential coefficients of Cohen and Bergstresser.[7] A close inspection of Table I reveals that there are three reasons for this dominance of V_{11}^s: (i) The energy gap is very sensitive to V_{11}^s, i.e., $\Delta E_g/\Delta V$ is large; (ii) V_{11}^s is the second largest pseudopotential coefficient; and (iii) the screening factor $(e^{-W}-1)$ is increasing approximately as $\sim G^2$. It is therefore clear that the disagreement between theory and experiment in Fig. 1 is not necessarily a firm result of the empirical pseudopotential method itself, but may result from the arbitrary truncation of the pseudopotential for $G^2 > 11$. To improve the theory one might introduce additional pseudopotential coefficients. Alternately, one might use the measured temperature dependence of the energy gap as input data to essentially fix V_{11}^s, thereby reducing the number of disposable parameters to five.

We thank Dr. Frank Herman for sending us a copy of his pseudopotential program, and Mrs. C. A. Lambert for performing the numerical calculations.

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[1] J. P. Walter, R. R. L. Zucca, M. L. Cohen, and Y. R. Shen, Phys. Rev. Letters 24, 102 (1970).

[2] J. L. Shay, Phys. Rev. B 2, 803 (1970).

[3] J. L. Shay and R. E. Nahory, Solid State Commun. 7, 945 (1969); R. E. Nahory and J. L. Shay, Phys. Rev. Letters 21, 1569 (1968).

[4] The temperature dependence of the energy gap determined from absorption-coefficient measurements [M. D. Sturge, Phys. Rev. 127, 768 (1962)] is not appreciably different from the photoreflectance values, although the latter are expected to be more precise near room temperature.

[5] C. Keffer, T. M. Hayes, and A. Bienenstock, Phys. Rev. Letters 21, 1676 (1968).

[6] This linear approximation to the shifts of energy gaps for small changes in potential coefficients has previously been employed to fit theoretical calculations to experimental data. See for example F. Herman, R. L. Kortum, C. D. Kuglin, and J. L. Shay, in *Proceedings of the II–VI Semiconducting Conference, Providence, Rhode Island* (Benjamin, New York, 1967), p. 503.

[7] M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966).