0000000044220077334957

Submitted to Physical Review Letters

LBL-3539
Preprint c. 1

# LOCAL-FIELD EFFECTS IN THE OPTICAL SPECTRUM OF SILICON

Steven G. Louie, James R. Chelikowsky, and Marvin L. Cohen

November, 1974

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

LBL-3539 c. 1

## 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.

0000000044220077534968



LBL-3539

# Local-Field Effects in the Optical Spectrum of Silicon*

Steven G. Louie,† James R. Chelikowsky and Marvin L. Cohen
Department of Physics, University of California
and
Inorganic Materials Research Division,
Lawrence Berkeley Laboratory, Berkeley, California 94720

Abstract

We have calculated the dielectric response matrix, $\varepsilon_{\underset{\sim}{G},\underset{\sim}{G}'}(\underset{\sim}{q}=0,\omega)$ for silicon and have obtained the macroscopic frequency dependent dielectric function. Contrary to recent calculations, local-field corrections do not shift the peak positions of the imaginary part of the dielectric function; further the calculated dielectric function is improved as compared to experiments at higher energies. In particular, agreement with measured energy-loss spectra is significantly better when local-field effects are included.

Recently, much effort has been made to understand the role of microscopic electric fields on various physical properties of crystalline solids.[1-13] Two recent Physical Review Letters[1,2] have been published on local-field

corrections to the optical spectrum of diamond; however, the two calculations give quite different results. By inverting the dielectric response matrix, Van Vechten and Martin,[1] using the pseudopotential method, and Hanke and Sham,[2] using a linear combination of atomic orbital (LCAO) method, have calculated the macroscopic dielectric function for diamond in the random phase approximation (RPA).[14] Van Vechten and Martin find that local-field effects shift the strength of the imaginary part of the dielectric function, $\varepsilon_2(\omega)$, to the energy region just above the main optical peak. This behavior increases the discrepancy between the calculated $\varepsilon_2(\omega)$ and experiment. In an attempt to improve agreement with experiment, Van Vechten and Martin included the effects of dynamical correlation in their calculation of $\varepsilon_2(\omega)$ via a one-parameter model. Hanke and Sham, on the other hand, find that local-field effects weaken the strength of $\varepsilon_2(\omega)$ up to energies 8 eV above the main optical peak and that the positions of the peaks in $\varepsilon_2(\omega)$ are shifted in the opposite direction needed to achieve good accord with experiment by approximately 0.5 eV. Hanke and Sham then include exchange effects (beyond the RPA) into their calculation of the macroscopic dielectric function and are able to achieve better agreement with experiment.

To gain some new insights into the effect of local-field corrections to optical spectra of covalent solids, we present here a calculation of the dielectric function of

silicon with local-field effects included. Using an extremely accurate band structure from the empirical pseudopotential method, we have calculated the RPA dielectric response matrix, $\varepsilon_{\underset{\sim}{G},\underset{\sim}{G}'}(q=0,\omega)$, for silicon and inverted it to obtain the macroscopic frequency dependent dielectric function. We find that (1) local-field corrections do not shift the peak positions of $\varepsilon_2(\omega)$ and that (2) local-field corrections do improve the calculated dielectric function as compared to experiments at energies higher than the main optical peak. In particular, agreement with measured energy-loss spectra is significantly better when local-field effects are included. Therefore with excitonic effects in the lower energies taken into considerations, which should enhance the strength of $\varepsilon_2(\omega)$,[15] it is not clear that either dynamical correlations or exchange effects are needed to obtain good agreement between the calculated and measured macroscopic dielectric function at least in the silicon case.

Within the linear response theory, a small perturbing electric field of frequency $\omega$ and wavevector $\underset{\sim}{q}+\underset{\sim}{G}$ in a crystal will establish responses with frequency $\omega$ and wavevectors $\underset{\sim}{q}+\underset{\sim}{G}'$, where $\underset{\sim}{G}$ and $\underset{\sim}{G}'$ are reciprocal lattice vectors. The microscopic fields of wavevectors $\underset{\sim}{q}+\underset{\sim}{G}'$ are generated from the applied perturbing field through umklapp processes. In the case of cubic crystals, the dielectric responses of the solid for longitudinal fields may be described by a matrix in $\underset{\sim}{G}$ and $\underset{\sim}{G}'$,[14]

$$\sum_{\underset{\sim}{G}'} \varepsilon_{\underset{\sim}{G},\underset{\sim}{G}'}(\underset{\sim}{q},\omega)E(\underset{\sim}{q}+\underset{\sim}{G}',\omega) = E_{pert}(\underset{\sim}{q}+\underset{\sim}{G},\omega) \ , \qquad (1)$$

where E is the total field in the crystal and $E_{pert}$ is the applied perturbing field. Microscopic-field effects (or local-field effects) are traditionally ignored by assuming the off-diagonal elements of the dielectric response matrix to be zero. However the off-diagonal elements can be important when considering local-field corrections to optical spectra,[1-3] plasmon dispersion in metals,[4,5] valence-electron density,[6] and lattice dynamics[7-11] in semiconductors and insulators.

In analyzing the optical spectrum, the incident light of frequency $\omega$ may be viewed as a perturbing field of vanishingly small wavevector. The macroscopic dielectric function is given by[14]

$$\varepsilon(\omega) = \lim_{\underset{\sim}{q}\to 0} \frac{1}{[\varepsilon^{-1}(\underset{\sim}{q},\omega)]_{\underset{\sim}{0},\underset{\sim}{0}}} \ , \qquad (2)$$

where $\varepsilon^{-1}$ is the inverse of the matrix $\varepsilon_{\underset{\sim}{G},\underset{\sim}{G}'}$. Adler and Wiser[14] have derived, within the RPA, the following expression for the dielectric response matrix[16]

$$\varepsilon_{\underset{\sim}{G},\underset{\sim}{G}'}(\underset{\sim}{q},\omega) = \delta_{\underset{\sim}{G},\underset{\sim}{G}'} - \frac{4\pi e^2}{\Omega|\underset{\sim}{q}+\underset{\sim}{G}||\underset{\sim}{q}+\underset{\sim}{G}'|} \sum_{\underset{\sim}{k}nn'} \frac{f_0[E_{n'}(\underset{\sim}{k}+\underset{\sim}{q})]-f_0[E_n(\underset{\sim}{k})]}{E_{n'}(\underset{\sim}{k}+\underset{\sim}{q})-E_n(\underset{\sim}{k})+\hbar\omega+i\hbar\alpha}$$

$$\times \langle \underset{\sim}{k}+\underset{\sim}{q},n'|e^{i(\underset{\sim}{q}+\underset{\sim}{G})\cdot\underset{\sim}{r}}|\underset{\sim}{k},n\rangle\langle \underset{\sim}{k},n|e^{-i(\underset{\sim}{q}+\underset{\sim}{G}')\cdot\underset{\sim}{r}}|\underset{\sim}{k}+\underset{\sim}{q},n'\rangle \ , \qquad (3)$$

where $\Omega$ is the crystal volume, $f_0$ is the Fermi-Dirac distribution function, and $|\underset{\sim}{k},n\rangle$ and $E_n(\underset{\sim}{k})$ are eigenstates and

eigenvalues of the unperturbed Hamiltonian. $\varepsilon_{\underset{\sim}{0},\underset{\sim}{0}}(\underset{\sim}{q},\omega)$ is just the usual Cohen-Ehrenreich dielectric function (no local-field effects).[17]

To evaluate the required matrix elements and eigenvalues in Eq. (3), we have calculated a band structure for silicon using the empirical pseudopotential method.[18] The resulting band structure[19] is in excellent agreement with the optical gaps and photoemission experiments. Each $\varepsilon_{\underset{\sim}{G},\underset{\sim}{G}'}(\underset{\sim}{q}=0,\omega)$ was evaluated in energy intervals of 0.125 eV up to 100 eV. The summation over wavevector was performed by evaluating the wavefunctions and eigenvalues on a grid of 308 $\underset{\sim}{k}$-points in the irreducible zone. The matrix size of the dielectric response matrix involved in the inversion for Eq. (2) was chosen to be 59 × 59, containing $\underset{\sim}{G}$-vectors through the set (222). Symmetry can be invoked to reduce the number of $\varepsilon_{\underset{\sim}{G},\underset{\sim}{G}'}$ elements which need be calculated to 72. Convergence of the macroscopic dielectric function was confirmed by inversion of $\varepsilon_{\underset{\sim}{G},\underset{\sim}{G}'}$ including sets of $\underset{\sim}{G}$-vectors through (111), (200), (220), (311), and (222) respectively.

In order to establish the accuracy of the calculated $\varepsilon_{\underset{\sim}{G},\underset{\sim}{G}'}$, we have tested our results using the sum rules as derived by Johnson,[20]

$$\int_0^\infty \omega \, \mathrm{Im}\, \varepsilon_{\underset{\sim}{G},\underset{\sim}{G}'}(\underset{\sim}{q},\omega)d\omega = \frac{\pi}{2}\,\omega_p^{\,2}\left(\frac{\rho(\underset{\sim}{G}-\underset{\sim}{G}')}{\rho(\underset{\sim}{0})}\right)\hat{e}(\underset{\sim}{q}+\underset{\sim}{G})\cdot\hat{e}(\underset{\sim}{q}+\underset{\sim}{G}') \ , \quad (4)$$

where $\omega_p^{\,2} = 4\pi ne^2/m$ is the plasma frequency, $\rho(\underset{\sim}{G})$ are the Fourier transforms of the valence-electron density, and

$\hat{e}(\underset{\sim}{q}+\underset{\sim}{G})$ is a unit vector in the $\underset{\sim}{q}+\underset{\sim}{G}$ direction. In Table I we list our calculated results for the specific cases $\underset{\sim}{G} = \underset{\sim}{G}'$ and $\underset{\sim}{G} = 0$, $\underset{\sim}{G}' \neq 0$. The integral appearing in Eq. (4) was evaluated over a 100 eV range in intervals of 0.125 eV. Our results demonstrate good internal consistency except for the diagonal elements for the higher $\underset{\sim}{G}$-vectors. This arises from the fact that Im $\varepsilon_{\underset{\sim}{G},\underset{\sim}{G}}(q=0,\omega)$ becomes more extended in frequency as $|\underset{\sim}{G}|$ increases and that the integrand in Eq. (4) is linearly weighted with frequency. Better results can be obtained if we extend our integrations beyond the 100 eV range. As far as the optical properties are concerned, this high energy behavior is unimportant, and our values for $\varepsilon_{\underset{\sim}{G},\underset{\sim}{G}'}$ in the region considered should be very accurate.

The calculated imaginary part of the macroscopic dielectric function with (Adler-Wiser) and without local-field (Cohen-Ehrenreich) corrections, $\varepsilon_2(\omega)$ and Im $\varepsilon_{\underset{\sim}{0},\underset{\sim}{0}}(\omega)$ respectively, is given in Fig. 1 together with the experimental measurement of Philipp and Ehrenreich.[21] From Fig. 1 we see that local-field corrections do not alter the peak positions, although they do alter the strength of the dielectric function. Compared with the usual Im $\varepsilon_{\underset{\sim}{0},\underset{\sim}{0}}(\omega)$, $\varepsilon_2(\omega)$ has less strength at energies below the main optical peak, thus increasing the discrepancy with experiment. At energies higher than the main optical peak, the strength of $\varepsilon_2(\omega)$ is reduced from that of Im $\varepsilon_{\underset{\sim}{0},\underset{\sim}{0}}(\omega)$ until approximately 7 eV. Beyond this point $\varepsilon_2(\omega)$ is larger than Im $\varepsilon_{\underset{\sim}{0},\underset{\sim}{0}}(\omega)$: an event which must transpire

if the well known sum rules[14] are to be satisfied. This behavior results in an overall improvement in $\varepsilon_2(\omega)$ at higher energies as compared with experiment. Excitonic effects, particularly on the lower energy side of the main optical peak, which are not included in our calculation, should further improve the agreement between our $\varepsilon_2(\omega)$ result and experiment in the low energy region. The effect of these electron-hole interactions tends to increase the oscillator strength, hence the strength of $\varepsilon_2(\omega)$, at the lower energies.

Another improvement of $\varepsilon(\omega)$ arising from local-field effects at higher energies is reflected in the calculated energy-loss spectrum of silicon as indicated in Fig. 2. We note a drastic decrease in the magnitude of the peak of $\mathrm{Im}\left(\frac{1}{\varepsilon(\omega)}\right)$ through the inclusion of local-field effects, and a shifting of the peak by approximately 1.2 eV to lower energies.[22] Both these effects result in significantly better agreement with experiments.[21,23] However, effects other than local-field corrections,[24] might also be responsible for at least some of the discrepancy between experiment and the calculated $\mathrm{Im}(1/\varepsilon_{\underset{\sim}{0}\underset{\sim}{0}}(\omega))$.

In conclusion we remark that there are now three calculations on the effect of local-field corrections to the optical spectra of covalent solids using the RPA formalism. All three calculations give different results indicating that there remains work to be done to establish firmly the influences of local-field effects. The calculations presented

here indicate that higher order corrections like exchange and dynamical correlation may not be as important as stated in Refs. 1 and 2.

We would like to thank Stanley J. Sramek and J. P. Walter for helpful discussions in the early stages of this work. Part of this work was done under the auspices of the Atomic Energy Commission.

## References

* Supported in part by the National Science Foundation Grant DMR72-03206-A02.

† National Science Foundation Graduate Fellow.

1. J. A. Van Vechten and R. M. Martin, Phys. Rev. Lett. 28, 446 (1972).
2. W. R. Hanke and L. J. Sham, Phys. Rev. Lett. 33, 582 (1974).
3. T. K. Bergstresser and G. W. Rubloff, Phys. Rev. Lett. 30, 794 (1973).
4. N. H. March and M. P. Tosi, Proc. R. Soc. A 330, 373 (1972).
5. K. C. Pandey, P. M. Platzman, P. Eisenberger, and E. N. Foo, Phys. Rev. B9, 5046 (1974).
6. E. Tosatti, C. Calandra, V. Bortolani, and C. M. Bertoni, J. Phys. C5, L299 (1972).
7. L. J. Sham, Phys. Rev. 188, 1431 (1969).
8. R. M. Pick, M. H. Cohen, and R. M. Martin, Phys. Rev. B1, 910 (1970).
9. R. M. Martin, Phys. Rev. 186, 871 (1969).
10. W. R. Hanke, Phys. Rev. B8, 4585, 4591 (1973).
11. C. M. Bertoni, V. Bortolani, C. Calandra, and E. Tosatti, Phys. Rev. Lett. 28, 1578 (1972) and Phys. Rev. B9, 1710 (1974).
12. D. L. Johnson, Phys. Rev. B9, 4475 (1974).
13. J. C. Inkson, J. Phys. C7, 1571 (1974).

14. S. L. Adler, Phys. Rev. 126, 413 (1962); N. Wiser, Phys. Rev. 129, 62 (1963).

15. J. C. Phillips, Solid State Phys. 18, 55 (1966).

16. Eq. (3) differs from the definition of $\varepsilon_{\underset{\sim}{G},\underset{\sim}{G}'}$ in Refs. 13-14 by a factor $|q+G|/|q+G'|$. This definition arises if electric fields are used in Eq. (1) instead of potentials. Both approaches lead to the same macroscopic dielectric function.

17. H. Ehrenreich and M. H. Cohen, Phys. Rev. 115, 786 (1959).

18. M. L. Cohen and V. Heine, Solid State Phys. 24, 37 (1970).

19. James R. Chelikowsky and Marvin L. Cohen, Phys. Rev. B (in press).

20. D. L. Johnson, Phys. Rev. B9, 4475 (1974).

21. H. R. Philipp and H. Ehrenreich, Phys. Rev. 129, 1550 (1963).

22. Our calculated $\mathrm{Im}(1/\varepsilon_{\underset{\sim}{0},\underset{\sim}{0}}(\omega))$ differs from that of J. P. Walter and M. L. Cohen, Phys. Rev. B5, 3101 (1972). Their result yielded a broader peak with a corresponding reduction in peak height. We feel that our result, which involved the use of a more accurate integration scheme for $\mathrm{Im}\ \varepsilon_{\underset{\sim}{0},\underset{\sim}{0}}(\omega)$ and did not involve the use of a tail function in obtaining $\mathrm{Re}\ \varepsilon_{\underset{\sim}{0},\underset{\sim}{0}}(\omega)$ from $\mathrm{Im}\ \varepsilon_{\underset{\sim}{0},\underset{\sim}{0}}(\omega)$, to be superior.

23. H. Dimigen, Z. Physik 165, 53 (1961).

24. For example, it is possible that the use of OPW matrix elements could also shift the position of the energy-loss

peak (M. Schlüter, private communication). Also see J. P. Van Dyke, Phys. Rev. B5, 1489 (1972).

Table I. Sum rules from Eq. (4) for $\varepsilon_{\underset{\sim}{0},\underset{\sim}{G}}$ and $\varepsilon_{\underset{\sim}{G},\underset{\sim}{G}'}$ in units of $(eV)^2$ in the limit $\underset{\sim}{q}\to 0$ along the $\hat{x}$-direction.

| $(\frac{a}{2\pi})\underset{\sim}{G}$ | $(\frac{a}{2\pi})\underset{\sim}{G}'$ | $\int\omega \text{ Im } \varepsilon_{\underset{\sim}{G},\underset{\sim}{G}'} d\omega$ | $\frac{\pi}{2}\,\omega_p^{\,2}\left(\frac{\rho(\underset{\sim}{G}-\underset{\sim}{G}')}{\rho(0)}\right)\hat{e}(\underset{\sim}{q}+\underset{\sim}{G})\cdot\hat{e}(\underset{\sim}{q}+\underset{\sim}{G}')$ |
|---|---|---|---|
| (000) | (000) | 415.6 | 433.5 |
| (111) | (111) | 431.6 | 433.5 |
| (200) | (200) | 430.1 | 433.5 |
| (220) | (220) | 403.2 | 433.5 |
| (311) | (311) | 311.8 | 433.5 |
| (222) | (222) | 278.4 | 433.5 |
| (000) | (111) | -50.9 | -54.7 |
| (000) | (200) | 0.0 | 0.0 |
| (000) | (220) | 11.5 | 10.3 |
| (000) | (311) | 21.6 | 20.2 |
| (000) | (131) | 7.2 | 6.7 |
| (000) | (222) | 15.5 | 15.0 |

Figure Captions

Figure 1. Calculated $\varepsilon_2(\omega)$ for Si, with (dashed curve) and without (dotted curve) local-field effects, compared with experiment (solid curve) from Ref. 21.

Figure 2. Calculated energy-loss spectra for Si, with (dashed curve) and without (dotted curve) local-field effects, compared with experiment (solid curve) from Ref. 21.

0 0 0 0 4 2 0 7 5 5 3

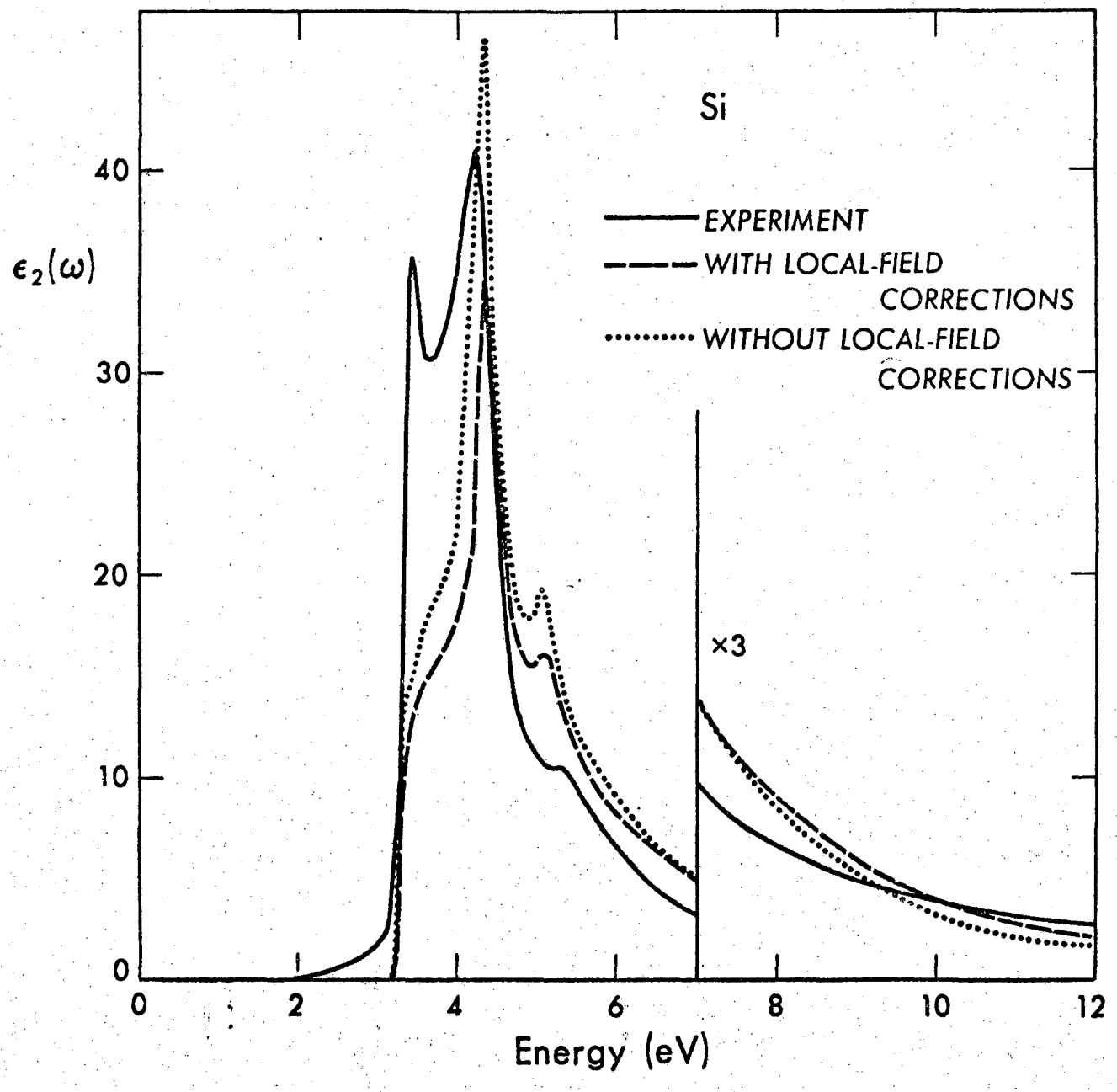


Fig 1

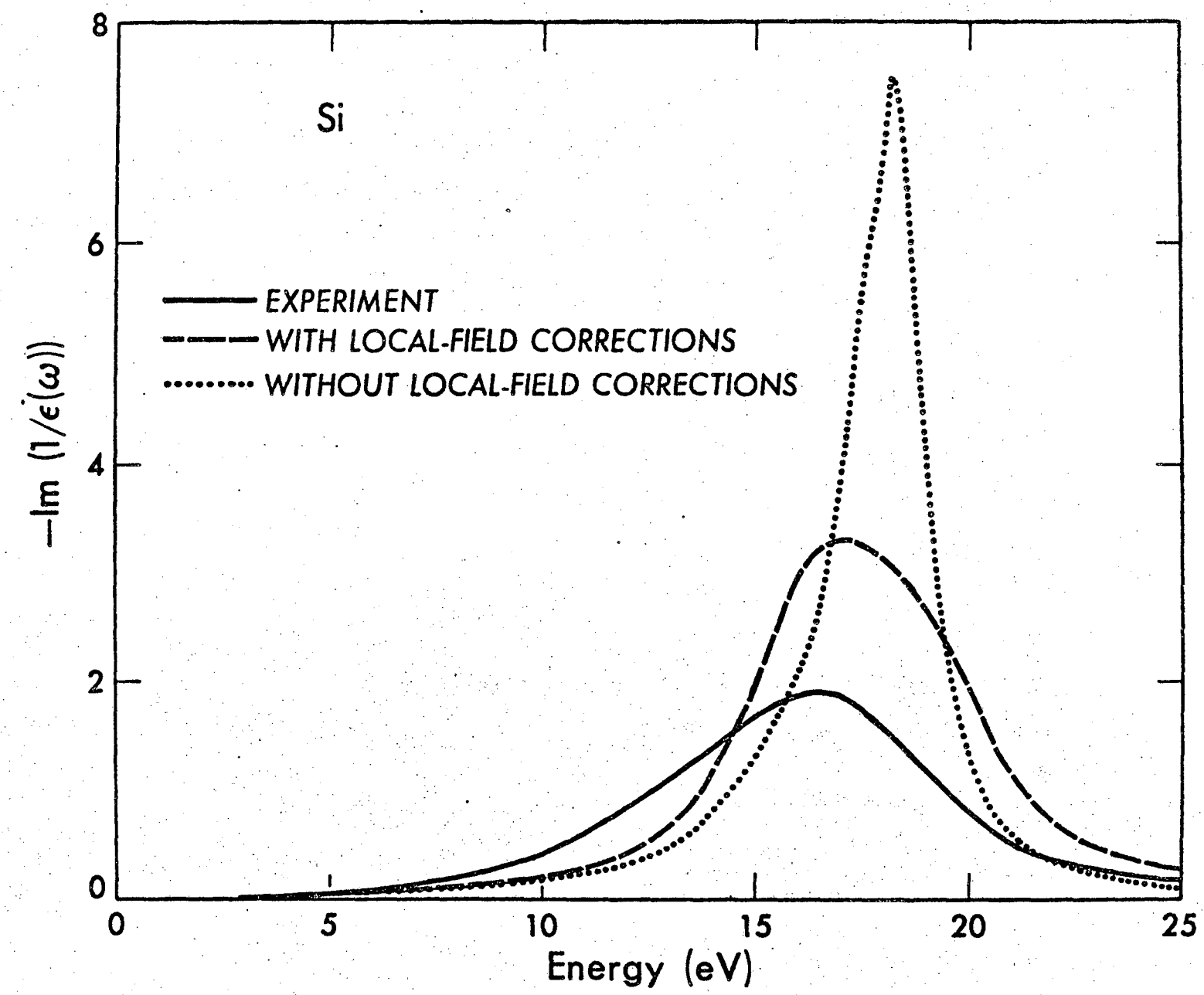
Si
EXPERIMENT
WITH LOCAL-FIELD CORRECTIONS
WITHOUT LOCAL-FIELD CORRECTIONS
$-\mathrm{Im}\ (1/\epsilon(\omega))$
Energy (eV)
0
2
4
6
8
0
5
10
15
20
25

Fig 2

0 0 0 0 4 2 0 7 5 3 4

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*