

²L. D. Landau, Zh. Eksp. Teor. Fiz. **32**, 59 (1957) [Sov. Phys. JETP **5**, 101 (1957)].

³B. E. Keen, P. W. Matthews, and J. Wilks, Phys. Lett. **5**, 5 (1963); D. S. Betts, B. E. Keen, and J. Wilks, Proc. Roy. Soc., Ser. A **289**, 34 (1965); I. J. Kirby and J. Wilks, Phys. Lett. **24A**, 60 (1966).

⁴W. R. Abel, A. C. Anderson, and J. C. Wheatley, Phys. Rev. Lett. **17**, 74 (1966).

⁵L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, London, 1959), p. 88.

⁶L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon, London, 1959), p. 130.

⁷L. R. Corruccini, J. S. Clarke, N. D. Mermin, and J. W. Wilkins, Phys. Rev. **180**, 225 (1969).

⁸M. J. Lea, A. R. Birks, P. M. Lee, and E. R. Dobbs, J. Phys. C **6**, L226 (1973).

⁹J. P. R. Bolton, in *Proceedings of the Fourteenth International Conference on Low Temperature Physics*

(American Elsevier, New York, 1975), Vol. 1, p. 115.

¹⁰H. A. Notarys, thesis, California Institute of Technology, 1969 (unpublished), available from University Microfilms, Ann Arbor, Michigan.

¹¹Cf. J. B. Ketterson, P. R. Roach, B. M. Abraham, and P. D. Roach, in *Quantum Statics and the Many-Body Problem*, edited by S. B. Trickey, W. P. Kirk, and J. W. Duffy (Plenum, New York, 1975).

¹²J. C. Wheatley, Rev. Mod. Phys. **47**, 415 (1975).

¹³E. Ostgaard, Phys. Rev. **187**, 371 (1969).

¹⁴M. P. Bertinat, D. S. Betts, D. F. Brewer, and G. J. Butterworth, J. Low Temp. Phys. **16**, 479 (1974).

¹⁵T. A. Alvesalo, H. K. Collan, M. T. Lopenon, O. V. Lounasmaa, and M. C. Veuro, J. Low Temp. Phys. **19**, 1 (1975).

¹⁶W. P. Halperin, C. N. Archie, F. B. Rasmussen, T. A. Alvesalo, and R. C. Richardson, Phys. Rev. B (to be published).

Pressure Dependence of Reflectivity of Se: Experimental Evidence for Large Local-Field Corrections*

Marc Kastner and R. R. Forberg

*Department of Physics and Center for Materials Science and Engineering,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

(Received 8 December 1975)

The pressure dependence of the reflectivity of trigonal and amorphous Se has been measured between 1.1 and 4.5 eV using a new technique. The results indicate that local-field corrections are large. Structure near 2 eV suggests a localized excitation in both the amorphous and the crystalline material.

Spectroscopic theories of chemical bonding in solids have proved to be powerful for predicting a wide range of properties of the $A^N B^{8-N}$ crystals (Ge, GaAs, etc.). The starting point of these theories is the identification of the bond strength with a spectroscopically determined energy. In Phillips's theory¹ this energy is determined by the dielectric constant, in Harrison's² theory it is the energy of the E_2 peak in the imaginary part of the dielectric function. In the case of the covalent $A^N B^{8-N}$ crystals, it may be reasonable to assume that microscopic fields and the modification of matrix elements resulting from exchange are small. (All of these effects will be called "local-field corrections" in this Letter.³) In such solids the charge density is fairly uniformly distributed around the atoms. On the other hand, in very ionic or molecular solids the charge density may be quite localized. In this case the determination of the bond strength from the spectroscopic energy is strongly modified by local-field corrections.⁴ Therefore, in order that spectroscopic theories of bonding can be extended to ionic and

molecular materials, local-field corrections must be better understood. This Letter presents the results of a new technique for studying local-field corrections in solids.

Since local-field corrections are density dependent, the pressure dependence of the optical properties of solids can indicate the size of these effects if the electrons' energy states are not strongly density dependent. For example, measurements of the pressure coefficient of the infrared refractive index for amorphous alloys containing Ge and Se show that Se-rich alloys obey the Lorenz-Lorentz relation,⁵ indicating large local-field effects in these materials. The pressure dependence of the reflectivity will reveal more information about local-field corrections, and since for Se these corrections are expected to be large, Se is an ideal material for study.

Early measurements of the reflectivity as a function of pressure were limited to observing energy shifts of the reflectivity peaks.⁶ Measuring the variation of the magnitude of the reflectivity is difficult because the refractive indices

of the pressure fluid and the window depend on pressure. We have developed a new experimental method with which we can measure fractional changes in reflectivity as small as one part in a thousand.⁷ Pressure-induced changes in the window transmission are canceled by measuring the real-time ratio of the reflectance of the sample to that of an aluminum mirror placed next to it in the pressure cell. The refractive index of helium, which is used as the pressure fluid, increases with increasing pressure, decreasing the reflectance from the sample. The reflectance change resulting from the density change of He is subtracted from the experimentally measured pressure coefficient, $(\Delta R/R\Delta P)_{\text{exp}}$, to give the corrected pressure coefficient, $\Delta R/R\Delta P$, as follows:

$$\frac{\Delta R}{R\Delta P} = \left(\frac{\Delta R}{R\Delta P}\right)_{\text{exp}} - \left(\frac{d \ln R}{dn_{\text{He}}}\right) \frac{\Delta n_{\text{He}}}{\Delta P}. \quad (1)$$

The second term on the right-hand side of Eq. (1) is calculated using the optical constants of the sample. $\Delta n_{\text{He}}/\Delta P$ is found from a separate measurement with diamond for which $\Delta R/R\Delta P = 9 \times 10^{-8}/\text{bar}$.

Measurements were made at room temperature on single crystals of trigonal Se (*c*-Se) grown by liquid-phase epitaxy on tellurium,⁸ and on samples of amorphous Se (*a*-Se) prepared by

splat cooling on polished Al. The reflectivity of Se was studied at pressures up to 4 kbar, at photon energies between 1 and 4.5 eV, and with the electric field of the photons polarized parallel and perpendicular to the *c* axis of the trigonal Se. The optic axis of the sapphire pressure window was aligned either parallel or perpendicular to the polarization direction.

Figure 1 shows the reflectivity *R*, its pressure coefficient $\Delta R/R\Delta P$, and the helium correction

$$\left(\frac{\Delta R}{R\Delta P}\right)_{\text{He}} = \left(\frac{d \ln R}{dn_{\text{He}}}\right) \frac{\Delta n_{\text{He}}}{\Delta P},$$

for *c*-Se with $\vec{E} \perp \vec{c}$ and $\vec{E} \parallel \vec{c}$, and for *a*-Se.⁹ In all cases the helium correction is seen to be negative and relatively featureless. The error in the helium correction is approximately 5% from the measurement of $\Delta n_{\text{He}}/\Delta P$, in addition to any errors in the optical constants of Se.¹⁰

It is remarkable that the average of $\Delta R/R\Delta P$ over the entire spectrum is large and positive for crystalline and amorphous Se. In each case this average value is almost the same as the zero-frequency extrapolation of $\Delta R/R\Delta P$. For *a*-Se, $\Delta R/R\Delta P$ at 1 eV is in good agreement with the results of Schneider and Vedam¹¹ who used an interferometric technique. The increase in the plasma frequency is insufficient to explain the large increase of the reflectivity with pres-

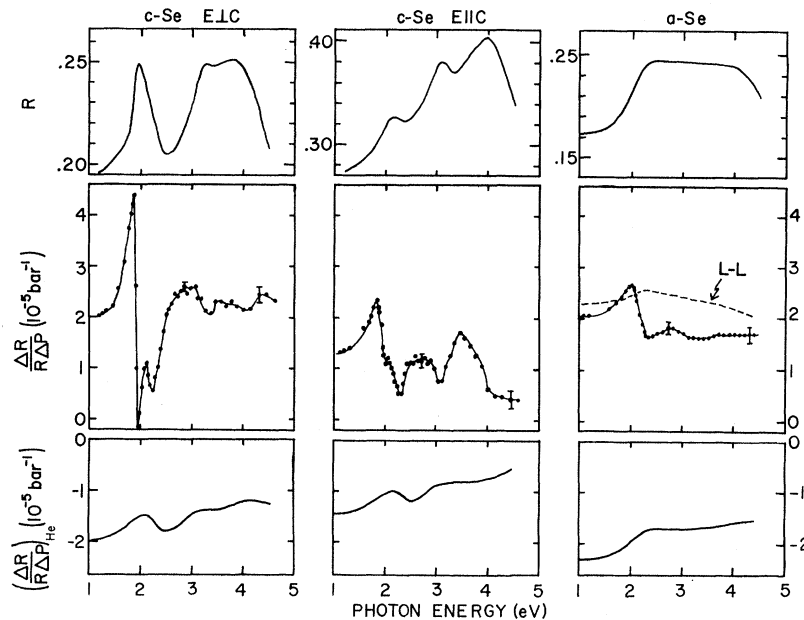


FIG. 1. The reflectivity, *R*, at atmospheric pressure; the fractional change of reflectivity per unit pressure, $\Delta R/R\Delta P$ (measured between 1 and 2 kbar); and the helium correction, $(\Delta R/R\Delta P)_{\text{He}}$, for crystalline and amorphous Se. The dashed curve is the Lorenz-Lorentz prediction for *a*-Se.

sure. Thus, a Drude relation, $\epsilon - 1 \sim \omega_p^2 \alpha$, predicts $\Delta R/R\Delta P = 2\kappa/\sqrt{\epsilon} = 0.8 \times 10^{-5} \text{ bar}^{-1}$, where κ is the compressibility, assuming that α , the polarizability, is independent of pressure.

To test whether the average increase of the reflectivity for *a*-Se is a consequence of local-field effects, we compare the experimental results with the prediction of the Lorenz-Lorentz relation:

$$(\epsilon - 1)/(\epsilon + 2) = (4\pi/3)N\alpha, \quad (2)$$

where ϵ and α are the complex dielectric function and polarizability, respectively, and N is the number density of polarizable centers in the solid.¹² Under the assumption that α is independent of density, then knowledge of ϵ at one density is sufficient to predict ϵ at all densities. Although there is local order in *a*-Se, the random orientation of the bonding plane relative to the applied field averages the local field correction, giving the same results as the isotropic case. Literature values¹⁰ of ϵ were used in this way to predict $\Delta R/R\Delta P$. The prediction for *a*-Se is plotted in Fig. 1. The agreement between the Lorenz-Lorentz prediction and experiment suggests that the average value of $\Delta R/R\Delta P$ is the result of local-field corrections.

The case of trigonal Se is much more complicated than that of *a*-Se. In the amorphous material it may be assumed that the anisotropy in the polarizability or local structure averages to zero. However, in order to find the relationship analogous to Eq. (2) for the crystal, a dipole sum must be carried out which includes the effects of both anisotropic α and the crystal structure. The Ewald method¹³ was used to calculate the matrix \underline{Q} which determines the electric field at a given site resulting from dipoles at all other sites. If \underline{p} is a nine-component vector representing the dipoles at the three atoms in the Se unit cell,

$$\underline{p} = \underline{\alpha}(\underline{E}_m + \underline{Q}\underline{p}). \quad (3)$$

Here \underline{E}_m is a nine-component vector representing the macroscopic electric field at each of the three atomic sites. Of course, this macroscopic field is the same at all sites. Both $\underline{\alpha}$ and \underline{Q} are 9×9 matrices. Equation (3) was solved numerically for \underline{p} , and the three dipoles were summed to obtain the polarization and hence the dielectric constant.

We have calculated the dielectric constant for both polarizations as a function of the magnitude and anisotropy of the polarizability in the low-photon-energy limit where both ϵ and $\underline{\alpha}$ are real.

It was assumed that the polarizability ellipsoid has its minor axis (α_b) in the plane containing the bonds to nearest neighbors, and its major axis (α_l) along the lone-pair orbital.⁵ Assuming that α_b and α_l are pressure independent, and knowing how the lattice constants and atomic position parameters change with hydrostatic pressure,¹⁴ we have also calculated $(\Delta R/R\Delta P)_\perp$ and $(\Delta R/R\Delta P)_\parallel$. The values $\alpha_l = 10.2 \pm 0.2 \text{ \AA}^3$ and $\alpha_b = 3.23 \pm 0.06 \text{ \AA}^3$ predict $\epsilon_\perp = 7.0 \pm 0.5$, $\epsilon_\parallel = 12.0 \pm 1.5$, $(\Delta R/R\Delta P)_\perp = (1.8 \pm 0.2) \times 10^{-5}/\text{bar}$, and $(\Delta R/R\Delta P)_\parallel = (1.3 \pm 0.2) \times 10^{-5}/\text{bar}$, all within experimental error. The anisotropy, $\alpha_b/\alpha_l = 0.315$, is reasonable. Since the average gap for the lone-pair electrons is half as large as that for the bonding electrons, and α is proportional to the inverse square of the gap, an anisotropy on the order of $\frac{1}{4}$ is expected.⁵ Thus, local-field effects are sufficient to explain the increase in reflectivity with pressure at low energy. Since the Lorenz-Lorentz relation predicts the increase in reflectivity over the entire energy range for *a*-Se, we expect that local-field corrections are also responsible for the increase in reflectivity at all energies for the crystal.

It is interesting to note that theoretically $\Delta R/R\Delta P$ does not approach zero in the limit of large photon energy. In that case $\epsilon = 1 - \omega_p^2/\omega^2$, where ω_p is the plasma frequency. This relation predicts $\Delta R/R\Delta P = 2\kappa = 2.0 \times 10^{-5} \text{ bar}^{-1}$ for *a*-Se.

The large structure in $\Delta R/R\Delta P$ for crystalline Se with $\vec{E} \perp \vec{c}$ (Fig. 1) is a consequence of the surprisingly large shift of the peak at 1.95 eV toward lower energy. As seen in Fig. 2, this peak shifts at a rate of $(4.0 \pm 0.2) \times 10^{-5} \text{ eV/bar}$. Concomitant with the shift of the peak is the growth of a shoulder on its high-energy side. For $\vec{E} \parallel \vec{c}$ (Fig. 3) the broad peak at 2.15 eV also shifts to lower energy, but at a lower rate, $(2.6 \pm 0.4) \times 10^{-5} \text{ eV/bar}$. In addition, the difference between the maximum and minimum in reflectance near 2.35 eV changes from $(2.3 \pm 0.5) \times 10^{-3}$ at atmospheric pressure to $(4.2 \pm 0.5) \times 10^{-3}$ at 3 kbar. For *a*-Se there is a structure in $\Delta R/R\Delta P$ which is similar to that for the crystal. In this case the structure corresponds to an increase of the reflectivity below the knee (see Fig. 1) near 2.2 eV and a smaller increase above it.

The energy shift of the 2-eV peaks of the crystal is unusual in two respects. First, the percentage change of the peak energies for the crystal (about 2%/kbar) is an order of magnitude larger than the largest lattice strain ($\Delta a/a = 0.3\%/kbar$). Typical peak shifts for $A^N B^{3-N}$ crystals are about 5 times the strains. Second, the peaks shift

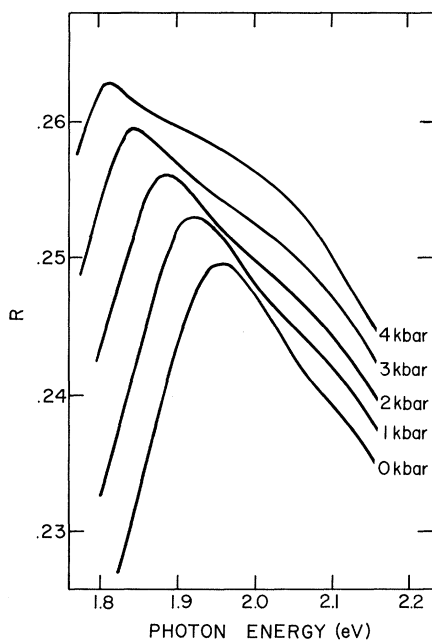


FIG. 2. Reflectivity at various pressures for c -Se with $\vec{E} \perp \vec{c}$.

twice as rapidly with pressure as the exponential tail of the absorption edge does. The absorption coefficient was measured in the range $1\text{--}10\text{ cm}^{-1}$. It was found to be exponential with a logarithmic derivative of about $10/\text{eV}$ in agreement with Henrion's¹⁵ higher absorption coefficient data. The edge shifts to lower energy at the rates $(1.83 \pm 0.02) \times 10^{-5}\text{ eV/bar}$ for $\vec{E} \perp \vec{c}$ and $(1.50 \pm 0.02) \times 10^{-5}\text{ eV/bar}$ for $\vec{E} \parallel \vec{c}$.¹⁶

The similarity of the $\Delta R/R\Delta P$ spectra for amorphous and crystalline Se near 2 eV suggests that the observed structures have a common origin. It is therefore unlikely that the low-energy peaks in the spectra for the crystal are the result of transitions between bands with a large difference in their deformation potentials. Instead, we suggest that these peaks arise from localized excitations between lone-pair and antibonding states which, although broadened, still exist in the amorphous material. Because the excitation is strongly polarized perpendicular to the chain axis, it might involve charge transfer between lone-pair states on one chain and antibonding states on neighboring chains.

All our results suggest that the electron charge density in Se is highly localized. Therefore, empirical band-structure calculations which are adjusted to fit the optical properties using the random-phase-approximation calculation of the dielectric function are in error because local-field

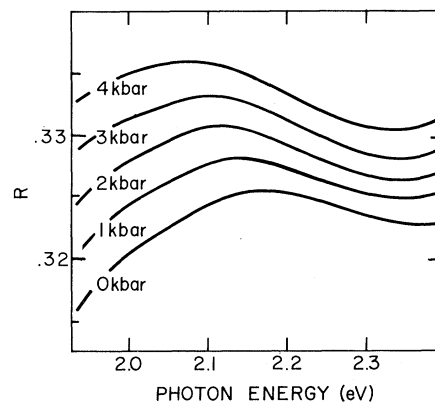


FIG. 3. Reflectivity at various pressures for c -Se with $\vec{E} \parallel \vec{c}$.

corrections are large.

We are extremely grateful to Dr. J. C. Thuilier for supplying samples of trigonal Se. We thank Professor J. D. Joannopoulos and Dr. G. G. Rubloff (I.B.M.) for helpful discussions.

*Work supported by National Science Foundation Grants No. DMR 73-02678 and No. GH 33635.

¹J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1974).

²W. A. Harrison and S. Ciraci, *Phys. Rev. B* **10**, 1516 (1974).

³W. Hanke and L. J. Sham, *Phys. Rev. Lett.* **33**, 582 (1974); S. G. Louie, J. R. Chelikowsky, and M. L. Cohen, *Phys. Rev. Lett.* **34**, 155 (1975).

⁴Of course, when the charge density is highly localized, the bond strength itself is affected.

⁵M. Kastner, *Phys. Rev. B* **7**, 5237 (1973), and *Phys. Rev. Lett.* **28**, 355 (1972).

⁶R. Zallen and W. Paul, *Phys. Rev.* **155**, 703 (1967).

⁷Details of the technique to be published.

⁸C. Lemerrier and J. M. Thuillier, *Mater. Res. Bull.* **1**, 109 (1966).

⁹The reflectivity we measure for c -Se is lower than that reported by others. This is a result of scattering from scratches and surface roughness. It is expected that this scattering does not introduce error in the measurement of $\Delta R/R\Delta P$ except at the highest photon energies.

¹⁰W. F. Koehler *et al.*, *J. Opt. Soc. Am.* **49**, 109 (1959); S. Tutihasi and I. Chen, *Phys. Rev.* **159**, 623 (1967).

¹¹W. C. Schneider and K. Vedam, *J. Opt. Soc. Am.* **60**, 800 (1970).

¹²T. K. Bergstresser and G. W. Rubloff, *Phys. Rev. Lett.* **30**, 794 (1974).

¹³M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford Univ. Press, Oxford, England, 1954).

¹⁴D. R. McCann and L. Cartz, *J. Appl. Phys.* **43**, 4473 (1972).

¹⁵W. Henrion, in *The Physics of Selenium and Tellurium*, edited by W. C. Cooper (Pergamon, New York, 1969).

¹⁶Earlier measurements of the effect of pressure on the minimum gap in *a*-Se were done by Robert S. Caldwell and H. Y. Fan, *Phys. Rev.* **114**, 664 (1959).

Critical Scattering from Piezoelectric Ferroelectrics

R. A. Cowley*

Brookhaven National Laboratory, † Upton, New York 11973

(Received 19 January 1976)

The complex asymmetric critical scattering observed in quasielastic neutron scattering measurements in KD_2PO_4 is explained as arising from the piezoelectric coupling between the acoustic waves and the ferroelectric fluctuations. Detailed calculations give good agreement with the available measurements. It is further proposed that this coupling provides a way of determining the atomic motions in the ferroelectric fluctuations and also leads to a change in the critical properties of these and related materials.

KD_2PO_4 (DKDP) is a piezoelectric material which undergoes a ferroelectric phase transition at 221 K. In the paraelectric phase, the fluctuations in the electric polarization are known¹⁻⁴ to be overdamped. Measurements¹⁻³ of the intensity of the neutrons scattered by the polarization fluctuations with wave vectors around reciprocal lattice points in the [010] zone gave contour maps of a shape characteristic of uniaxial ferroelectrics; the fluctuations with wave vectors along the ferroelectric axis [001] are suppressed by the macroscopic electric field. Similar measurements² around reciprocal lattice points in the [001] zone gave contour maps showing a complex structure, Fig. 1, the origin of which has not been explained. In this Letter it is shown that this pattern results from the piezoelectric coupling and interference between the acoustic waves and the electric polarization fluctuations. It is proposed that further measurements of these effects provide a particularly sensitive way of determining the atomic motions in the ferroelectric fluctuations which

avoids some of the difficulties inherent in the more conventional methods. The coupling between the acoustic waves and the ferroelectric fluctuations also modifies the critical behavior at the ferroelectric transition and so must be included in any detailed comparison between experiment and theory for these materials. Finally, similar effects may occur at all structural phase transitions where the order parameter is linearly coupled to a homogeneous deformation.

The neutron scattering in the [010] zone from the electric polarization fluctuations of wave vector \vec{q} could be described as the scattering from an overdamped phonon mode.³ Results similar to those obtained below can be obtained if the fluctuations are described by a tunneling mode instead of a phonon mode. The scattered intensity for a wave-vector transfer \vec{Q} and a frequency ω is determined by ($k_B T \gg \hbar\omega$)

$$S(\vec{Q}, \omega) = (Nk_B T / \pi\omega) |F_0(\vec{Q})|^2 \text{Im} [G_{00}(\vec{q}, \omega)],$$

where the response function is given for small $|\vec{q}|$ by

$$G_{00}(\vec{q}, \omega)^{-1} = M_0(\vec{q}, \omega) = \omega_0^2 + Cq_z^2/q^2 + B[(ag_x)^2 + (ag_y)^2 + (cq_z)^2] - i\omega\Gamma, \quad (1)$$

where the damping constant Γ is larger than any of the real terms in M_0 , and B and C are temperature-independent constants, while

$$\omega_0^2 = A(T - T_C^F),$$

with T_C^F the free-crystal Curie temperature. The structure factor for the polarization fluctuations is given by

$$F_0(\vec{Q}) = \sum_K b_K \exp[-W_K(\vec{Q})] \vec{Q} \cdot \vec{e}(K, \vec{q}) \exp(i\vec{\tau} \cdot \vec{R}_K), \quad (2)$$

where b_K , \vec{R}_K , $W_K(\vec{Q})$, and $\vec{e}(K, \vec{q})$ are the neutron coherent scattering length, position in the unit cell, Debye-Waller factor, and eigenvector of the K th atom in the unit cell. $\vec{\tau}$ is the reciprocal lattice vec-