approximately 10^2 times faster than the classical value based on the anomalous collision frequency. Studies on the fluctuation level are underway.

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*On leave from the Department of Electrical Engineering, Utsunomiya University, Utsunomiya, Japan.

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Theoretical Study of the Electronic Properties of Trigonal Se under Pressure

H. Wendel,* Richard M. Martin, and D. J. Chadi
Xerox Palo Alto Research Center, Palo Alto, California 94304

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Pseudopotential calculations for the pressure dependence of the dielectric constants and energy-band structure of trigonal Se are presented. The calculations explain recent experimental observations of a strong pressure dependence for the optic spectra of Se. It is shown that interchain interactions and not local-field corrections are most important in describing the pressure data.

The pressure dependence of the optical properties of solids is determined by (i) changes in electronic states as a function of the spacings between atoms and (ii) explicit density dependence of the dielectric response function, for example, local-field effects.[1] Of particular interest in this respect are molecularlike solids in which the density can be increased greatly with pressure. Recently measurements of the reflectivity spectrum of trigonal Se under pressure have been reported by Kastner and Forberg (KF).[2] They interpreted their results in a molecular model, i.e., they completely neglected (i), and concluded that the large pressure-induced changes could be explained only by local-field effects included in (ii). In this Letter, we examine the electronic bands of Se under pressure and we show that the resulting optical properties, calculated with no local-field corrections, explain the results of KF. We find that the large effects observed by KF are, in fact, precursors of the transition of Se to a metallic nonmolecular structure, which occurs at 130 kbar.[3] We further argue why one expects a band picture for the electronic states to be adequate and local-field corrections to be small in Se.

Trigonal Se is a chainlike crystal, in which each atom is strongly bound to two nearest neighbors to form helical chains. The chains are packed together in a hexagonal pattern with each atom having weaker interactions with four moredistant neighbors on different chains. The primary effect of pressure is to bring the chains closer together, increasing the density and the interchain interactions.

For the investigation of the Se band structure under pressure, presented in this Letter and discussed in more detail elsewhere,[4] we employ an empirical pseudopotential based on an ionic model potential proposed by Appelbaum and Hamann (AH)[5,6] for Se. The total pseudopotential is the linearly screened AH ionic potential; its Fourier transform is given by

$$V_{\text{total}}(\vec{G}) = v_{\text{ion}}(\vec{G})S(\vec{G})/\epsilon(\vec{G}), \tag{1}$$

where $\epsilon(\vec{G})$ is the linear response function of a uniform electron gas (with assumed $\rho^{1/3}$ exchange and correlation interaction[7]) with its exchange parameter chosen to be 0.706 65 for Se,[8] and $S(\vec{G})$ is the usual structure factor. This form for the total potential was shown to be an accurate representation of the self-consistent potential of Si by AH.[5] It also leads to accurate predictions for the bands of Si under pressure.[9] Here we apply the same approximation to study the pressure dependence of the electronic states in Se.

In order to get good overall agreement with experiment for the bands of Se at zero pressure, we have adjusted the parameters in V_{ion}.[5] Here we use $\alpha = 0.57$, $v_1 = 2.505$, and $v_2 = -2.0$. The resulting band structure is shown in Fig. 1. The bands near the Fermi energy agree to within ± 0.1 eV with those of Sandrock[10] and the lowest direct gap is at the H point of the Brillouin zone, in agreement with experiment.[11] In the lower valence-band region, our results are closer to those of Joannopoulos, Schluter, and Cohen[12] who fitted their density of states to photoemission data. The imaginary part of the frequency-dependent dielectric constant, $\epsilon_2(\omega)$, was calculated within the random phase approximation (RPA) and found to be in close correspondence with Ref. 10. For the static dielectric constant, $\epsilon_1(0)$, for light polarized parallel (∥) and perpendicular (⊥) to the c axis, we obtain $\epsilon^{\perp} = 6.85$ and $\epsilon^{\parallel} = 10.34$ which compare well with the experimental values of 6.6 and 10.6, respectively,[13] as shown in Table I.

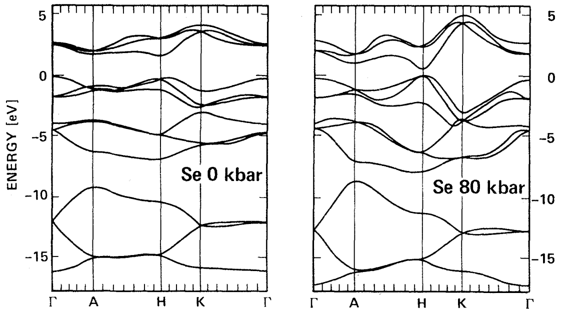

FIG. 1. Band structure at 0 and 80 kbar as calculated with the potential of Eq. (1).

We have also studied the variation of the band structure under pressure using the modified AH ionic potential. The changes with pressure are due to changes in reciprocal-lattice vectors, the inverse volume factor that enters the Fourier transform, and the volume dependence of $\epsilon(\vec{G})$ in Eq. (1). Changes in the unit-cell dimensions a and c at low pressures were obtained from the data of Martin, Fieldly, and Richter[14] and of McCann *et al.*[15] These give compressibilities that differ by a factor of ~ 2.[16] At low pressures, the nearest-neighbor distance remains very nearly constant.

In order to compare our results with experiment,[2] we concentrate in this Letter on the low-energy region of the optical spectrum between 1.4 and 2.4 eV. KF have attributed the unusually large energy shift (with pressure) of the reflectivity peak and the increase in the reflectance as arising from LF corrections. The structure in the reflectivity spectrum in this energy range is mainly due to transitions near the H point.[10] The calculated $\epsilon_2^{\perp}$ and $\epsilon_2^{\parallel}$ spectra are compared in Fig. 2 for 0 and 10 kbars of pressure, where we have made use of the linear compressibilities $da/adp = -3.19 \times 10^{-3}$ kbar^{-1} and $dc/cdp = 1.43 \times 10^{-3}$ kbar^{-1}. Let us first discuss the $\epsilon_2^{\parallel}$ spectrum shown in Fig. 2. At zero pressure we find a shoulder at about 2.28 eV. In the reflectivity

TABLE I. Comparison of optical properties at zero pressure for experiment and the theory presented in this Letter. $E^{\parallel}$ depicts the energy (in eV) of the peak in the $\epsilon_2^{\parallel}$ spectrum (Fig. 2). $E_1^{\perp}$ and $E_2^{\perp}$ correspond to the two peaks in the $\epsilon_2^{\perp}$ spectrum which are not resolved in the experiment. $\epsilon_{\perp,\parallel}$ represent the dielectric constant $\epsilon_1(\omega)$ in the limit of $\omega = 0$. The experimental values for peak positions are obtained from reflectivity measurements.

	Exp.	Theory
$E^{\parallel}$	3.15[a]	2.28
$E_1^{\perp}$		2.0
$E_2^{\perp}$	1.95[a]	2.23
$\epsilon^{\parallel}$	10.6[b]	10.34
$\epsilon^{\perp}$	6.6[b]	6.85

[a] Ref. 2. [b] Ref. 13.

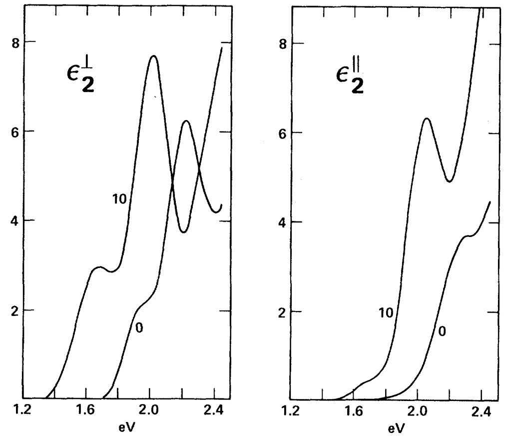

FIG. 2. Calculated $\epsilon_2^{\perp}$ and $\epsilon_2^{\parallel}$ spectra of Se for pressures of 0 and 10 kbar, respectively, using the compressibilities in Ref. 15. Note the shifts in peak positions to lower energy and increase in the integrated intensities under pressure.

TABLE II. Comparison of the experimental and theoretical pressure coefficients for the quantities in Table I. Columns 2 and 3 display the theoretical results derived from the compressibilities of Refs. 14 and 15, respectively. The coefficients for the energies are in 10^{-2} eV/kbar. The logarithmic coefficients of the dielectric constant are in 10^{-2} kbar^{-1}. The experimental values are from Ref. 2.

	Observed	Calculated	
$dE^{\parallel}/dp$	-2.6 ± 0.4	-4.14	-2.3
$dE_1^{\perp}/dp$	-4.0 ± 0.2	-6.66	-3.7
$dE_2^{\perp}/dp$	⋯	-3.96	-2.2
$d\ln\epsilon^{\parallel}/dp$	1.5	6.39	3.59
$d\ln\epsilon^{\perp}/dp$	2.2	6.9	3.77

spectrum KF find a peak at 2.15 eV.[2] Since we adjusted the overall features of the band structure and not exclusively the gaps we consider this difference as unimportant. Under pressure we find a clearly resolved peak with its maximum at 2.05 eV (Fig. 2). The pressure coefficient derived from this energy shift is large in agreement with experiment as shown in Table II. We also find an increase in the integrated intensity of the peak. Since the structure in both $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ shift to lower energy with pressure in this energy range and the peaks increase strongly in magnitude, the peak in the reflectivity spectrum also behaves in the same way.[17] Our calculation therefore gives the most important experimental features without the inclusion of any local-field effects.

The low-energy structure of the $\epsilon_2^{\perp}$ spectrum (Fig. 2) at zero pressure consists of a peak at 2.23 eV and a shoulder at 2.0 eV which arises from transitions near the H point of the Brillouin zone. We find that under pressure the two structures can be resolved as two separate peaks at 1.63 and 2.0 eV. This occurs because of the larger pressure dependence of the lower-energy structure. These results are also consistent with those of KF: At zero pressure they find a maximum at 1.95 eV[3] which at room temperature has been shown to be the remnant of an exciton.[18] The exciton is associated with the transition at the H point and its energy is smaller than the direct gap. The exciton binding energy does not change much with pressure. Therefore, the experimental pressure coefficient of the reflectivity peak has to be compared with that of the lowest-energy peak in the calculation. Table II shows that our calculation does explain the large pressure dependence of this peak. The appearance of a two-peak structure with pressure (Fig. 2) is also consistent with experiment which shows the growth of a shoulder at the high-energy side of the reflectivity peak[2] as the pressure is increased.

We have also calculated the low-frequency dielectric constants as a function of the lattice parameters. The resulting pressure derivatives using the two sets of compressibilities[14,15] are given in Table II. We find that both $\epsilon^{\perp}$ and $\epsilon^{\parallel}$ increase rapidly with pressure and the ratio $\epsilon^{\parallel}/\epsilon^{\perp}$ decreases slightly. The increase in both $\epsilon^{\parallel}$ and $\epsilon^{\perp}$ shows unambiguously the decrease in the average electronic gaps with pressure and the increased polarizability arising from the enhancement of the interchain interactions. The pressure dependence we find with no local-field effects is even larger than that found by extrapolating the data of KF to zero frequency as shown in Table II. Considering the uncertainties in the compressibilities and the extrapolated experimental data, we believe the agreement is satisfactory.

We also show in Fig. 1 our calculated bands for Se at 80 kbar based on lattice constants and internal parameters determined from recent x-ray measurement.[19] A comparison of the 0 and 80 kbar calculations clearly demonstrates the strong effect of pressure on interchain bonding. The dispersion in the valence and conduction bands along Γ-A (Γ-K or A-H) is a good measure of the intrachain (interchain) interactions. Whereas there is only a small change (about 25%) in the top valence and lower conduction bandwidths from Γ to

A with a pressure of 80 kbar there is a large (110–150%) increase in the Γ–K or A–H bandwidths. These results are consistent with charge density calculations which show the effect of nearest-neighbor chain distance on the interchain bonding charge.[12] Our high-pressure band structure for Se resembles the free-electron band structure of a hexagonal metal[20]: There is a large gap at K and a near degeneracy of valence and conduction states at H. These changes in the band structure are a precursor to a matallic phase which occurs at 130 kbar.[3] At 80-kbar pressures Se is nearly isotropic. Its band structure resembles that of Te[12] at zero pressure.

Let us now consider the adequacy of our band calculations for Se and the reasons why local-field effects should not modify greatly the dielectric function. The fundamental issue which must be addressed is the degree of localization of the electronic states. In a molecular system of low density, excited electronic states are localized and are greatly influenced by intramolecular exchange and correlation.[21] In that case, intramolecular dipolar interactions lead to a Lorenz-Lorentz–type expression[2] for the dielectric function ϵ. The analysis by KF of their experimental results is based upon such a picture. For high densities, however, overlap of wave functions between the molecules leads to the bandlike electronic states in which exchange, correlation, and local-field effects are all reduced. The only other covalent solids for which these effects have been examined in detail are silicon and diamond. In those cases, ordinary RPA band calculations for $\epsilon(\omega)$ are found to be very close to the final results for two reasons: (1) The wave functions are sufficiently delocalized; and (2) the large dielectric screening greatly reduces effects of exchange and correlation.[1] We believe these results should also apply to trigonal Se because charge density calculations[12] and the magnitude of ϵ indicate Se to be comparable to silicon and diamond.

In conclusion, we have shown that an empirical pseudopotential with a simple functional form both in real and reciprocal space[5] and a simple physical meaning describes the electronic properties of trigonal Se at zero and finite pressures. We find that the chains of Se cannot be seen as noninteracting molecular units with highly localized charge distributions. Instead, interchain overlap is important and an ordinary electronic band picture applies. The importance of interchain interaction shows up especially under hydrostatic pressure: A fractional change in the interchain distance causes an order-of-magnitude larger fractional change in typical electronic band gaps. Thus the assumption made in Ref. 2 that the electronic states are not strongly pressure-dependent (i.e., not strongly density-dependent) is invalid. Our results explain the effects observed experimentally.[2] We conclude that RPA band calculations with no local-field effects are qualitatively correct for trigonal Se and that no great modifications are caused by exchange, correlation, or local fields.

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Theory of Pressure Dependence of the Density of States and Reflectivity of Selenium

J. D. Joannopoulos,*† Th. Starkloff,‡ and Marc Kastner§

Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 29 November 1976)

The pressure dependence of the density of states and the reflectivity of trigonal Se is calculated using a new self-consistent pseudopotential technique. The results show that pressure-dependent reflectivity experiments may be interpreted without the need for microscopic fields.

We present the first theoretical calculation using a self-consistent $X\alpha$ transition-state[1,2] pseudopotential[3] formalism for a crystal. This formalism is applied to the study of the pressure dependence of the electronic density of states and reflectivity of trigonal Se.

In a recent Letter,[4] reflectivity measurements (from 1 to 4.5 eV) of Se under pressure (up to 4 kbar) revealed two interesting results: firstly, an unexpected large increase in the reflectivity everywhere; and secondly, a large shift of the lowest-energy reflectivity peak towards lower energies.[5] The average increase in reflectivity and the shift of the peak are given in Table I in the first and second rows, respectively. It was suggested at that time that this increase may be interpreted in terms of microscopic-field (or local-field) corrections and that the large shift was a result of rather localized excitations near the optical gap.

In order to investigate these results theoretically, it is very important to formulate a theory which is self-consistent and as close to first principles as possible. There are three reasons for this. Firstly, self-consistency is important because of the strongly anisotropic and rather large linear compressibilities[6-8] of Se (in comparison with typical semiconductors like Si). The change in interchain distance is about an order of magnitude larger than the change in intrachain distance. Thus, one would expect the resulting redistribution of charge under pressure to have a nonnegligible effect on the screening potential. Secondly, there have been many fitted band-structure calculations[9-15] for trigonal Se which give varying results. In general, band structures which are fitted to the density of states do not reproduce the optical properties very well and vice versa. Finally, since experimental optical spectra already include local-field effects (whose strengths for Se are *a priori* unknown) a band structure *fitted to these experimental properties* would necessitate the rather involved calculation of the dielectric response *including* local fields. A first-principles–like band structure, however, is not fitted to the excitations of the solid and can, therefore, be used to determine the dielectric function in the absence of local fields. This allows one to study those changes in the reflectivity that are caused only by the pressure-induced changes in band structure and wave functions.

The theory which we propose is based on a self-consistent pseudopotential formalism using $X\alpha$ exchange and an extension of the transition-state idea[2] from an atom to a crystal. Briefly, the theory can be divided into three parts. The first part involves the method used to generate the

TABLE I. Comparison of pressure dependence of theoretical and experimental observables (in 10^{-5} eV/bar).

	$\vec{E}\perp\vec{c}$		$\vec{E}\parallel\vec{c}$	
	Theor.	Expt.	Theor.	Expt.
$\langle\Delta\ln R/\Delta P\rangle$[a]	2.1	2.2	1.3	1.2
$\Delta E_R/\Delta P$	3.0	4.0 ± 0.2	3.0	2.6 ± 0.4
$\Delta E_g{}^d/\Delta P$	3.9[b]	···	3.9[b]	···
$\Delta E_g{}^i/\Delta P$	1.8[c]	1.83 ± 0.02	1.8[c]	1.50 ± 0.02
	2.4	···	2.4[d]	···

[a] Average taken from 1 to 4.5 eV in units of 10^{-5}/bar.

[b] $H_3 \rightarrow H_1$.

[c] $M_2 \rightarrow A_1$.

[d] $M_2 \rightarrow H_1$.