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

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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<sup>1,2</sup> pseudopotential<sup>3</sup> 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,<sup>4</sup> 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.<sup>5</sup> 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<sup>6-8</sup> 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<sup>9-15</sup> 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<sup>2</sup> 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	$4.0 \pm 0.2$	3.0	$2.6 \pm 0.4$
$\Delta E_g^d / \Delta P$	$3.9^b$	...	$3.9^b$	...
$\Delta E_g^i / \Delta P$	$1.8^c$	$1.83 \pm 0.02$	$1.8^c$	$1.50 \pm 0.02$
	2.4	...	$2.4^d$	...

<sup>a</sup>Average taken from 1 to 4.5 eV in units of  $10^{-5}$ /bar.

<sup>b</sup> $H_3 \rightarrow H_1$ .

<sup>c</sup> $M_2 \rightarrow A_1$ .

<sup>d</sup> $M_2 \rightarrow H_1$ .

bare-ion pseudopotential. The bare-ion pseudopotential is generated by first taking the self-consistent  $X\alpha$  potential of the neutral atom<sup>2</sup> and subtracting off those parts of the screening potential which arise from the valence electrons screening themselves. The resulting potential is transformed into a pseudopotential by setting it effectively equal to zero<sup>16</sup> inside a cutoff radius  $r_c$  so that one obtains an empty-core-like *ion pseudopotential*. The parameter  $r_c$  ( $r_c = 0.96$  a.u.) is chosen by self-consistently screening this ion pseudopotential (using the same functional form for the screening potential as in the original  $X\alpha$  calculation) and comparing the  $s$  and  $p$  valence energies of the *neutral* pseudo-atom with the corresponding  $X\alpha$  energies of the full *neutral* atom (i.e., including all the core electrons). Without further fitting, one reproduces all the  $s$ ,  $p$ , and (unoccupied)  $d$  energies and wave functions for all the ionic states of the atom *within 1%*, except for the  $\text{Se}^{6+}$  core energies which are obtained within 3%. The fit of the pseudopotential to  $X\alpha$  eigenenergies is justified by the very good agreement between the results of  $X\alpha$  calculations and experimental term values,<sup>2,17</sup> and permits the comparison of wave functions.

The second part of the theory involves the calculation of energies and wave functions for the *crystal*. This is accomplished in a self-consistent manner by using procedures similar to those employed by others.<sup>18,19</sup> The crystalline Schrödinger equation is solved with the bare-ion pseudopotential; and charge densities  $\rho(\vec{r})$ , are calculated. These densities, in turn, are used to compute a screening potential which has the same functional form as in the pseudo-atom. This potential is then added to the bare-ion pseudopotential resulting in a new trial potential. The process is repeated until self-consistency is achieved. Since this procedure involves no fitting to crystalline data and only minimal fitting to the atom, this calculation can be considered as being first-principles-like.

Finally, the third part of the theory is concerned with the transition-state<sup>1,2</sup> aspect of the screening potential. The eigenvalues of a Hamiltonian with the  $X\alpha$  form,  $\alpha[(81/\pi)\rho(\vec{r})]^{1/3}$ , for the exchange and correlation do not obey Koopmans's Theorem. Therefore, the proper way to compare theory and experiment is through a transition-state calculation. This involves fractional occupation numbers in the screening and thus contains average final-state relaxation effects. Fortunately good agreement, however, is often ob-

tained by taking  $\alpha = 1$  *without the transition state*, and by assuming Koopmans's Theorem as being still valid.<sup>2,17</sup> In our calculation, we use  $\alpha = 0.7064$  which reproduces the total Hartree-Fock energy of the neutral atom.<sup>20</sup> The localized nature of the electrons in trigonal Se suggests a treatment of the transition state in the crystal similar to that in the atom. This is accomplished by including a fractional occupation number in the average screening for each group of triplet bands involved in the transition.

As a test for the accuracy of our theory, we compare it with the *ab initio* self-consistent orthogonalized-plane-wave band-structure calculation by Krusius, von Boehm, and Stubb.<sup>21</sup> We find close quantitative agreement.

To apply our theory to study Se under pressure we use the compressibility measurements of McCann and co-workers<sup>6,7</sup> to determine the lattice constants. The literature also contains another set of compressibilities<sup>8,22,23</sup> which differ from McCann's by almost a factor of 2. Recently, however, the latter measurements have been shown to be inapplicable to trigonal Se since the samples may have included large amounts of amorphous Se.<sup>24</sup>

The results of our theory for the reflectivity are shown in Fig. 1. At the top of the figure we show experimental<sup>25,26</sup> results at 0 kbar for  $\vec{E} \perp \vec{c}$  and  $\vec{E} \parallel \vec{c}$ . The spectra show a small peak near 2 eV and a broader peak around 4 eV for both polarizations. In addition, there is an excitonlike peak

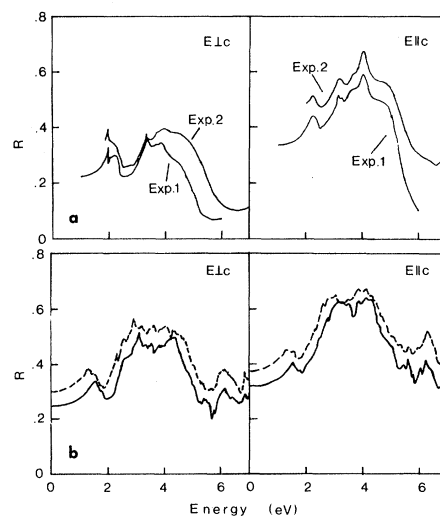


FIG. 1. (a) Experimental reflectivity spectra (Experiment 1, Ref. 25; and Experiment 2, Ref. 26) at 0 kbar for  $\vec{E} \perp \vec{c}$  and  $\vec{E} \parallel \vec{c}$ . (b) Theoretical reflectivities at 0 (solid line) and 8 kbar (dashed line) for  $\vec{E} \perp \vec{c}$  and  $\vec{E} \parallel \vec{c}$ .

below 2 eV in  $\vec{E} \perp \vec{c}$ . The theoretical reflectivities at 0 (solid line) and 8 kbar (dashed line) for  $\vec{E} \perp \vec{c}$  and  $\vec{E} \parallel \vec{c}$  are shown in Fig. 1(b). A comparison of Figs. 1(a) and 1(b) shows that the zero-pressure calculations are in fairly good agreement with the experiments. The main discrepancy lies in an overall shift of the theoretical results to lower energies by about 0.5 eV. The pressure-induced changes in the reflectivity, however, are insensitive to this shift and are in excellent agreement with experiment. Both the overall increase in reflectivity and the unexpected shift of the lowest-energy reflectivity peak are reproduced.

The doublet structure in the lowest-energy theoretical reflectivity peak arises from transitions around  $H_3 \rightarrow H_1$  and  $M_2 \rightarrow M_1$ . The pressure dependence of this peak  $\Delta E_R / \Delta P$  is given in Table I. The only discrepancy is with the value of the pressure dependence for the experimental  $\vec{E} \perp \vec{c}$  peak which is *excitonlike*. On the other hand, this experimental value is in good agreement with the pressure dependence  $\Delta E_g^d / \Delta P$  of the minimum direct gap as shown in Table I. This is strong evidence, therefore, that the peak observed experimentally for  $\vec{E} \perp \vec{c}$  arises from an exciton bound to the direct gap.<sup>27,28</sup>

From our band-structure calculation there are two minimum indirect gaps at  $M_2 \rightarrow A_1$  and  $M_2 \rightarrow H_1$  which are almost equal. The pressure measurements, however, suggest that the minimum indirect gap is in fact at  $M_2 \rightarrow A_1$ . This is shown in Table I where we compare the pressure dependence  $\Delta E_g^i / \Delta P$  of the theoretical indirect gaps with the pressure dependence deduced from absorption-tail studies.<sup>4</sup> It is interesting to contrast this assignment to recent work by Lingelbach *et al.*<sup>28</sup> These authors interpreted their electroreflectance measurements in terms of theoretical Korringa-Kohn-Rostoker (KKR) band-structure calculations.<sup>11,12</sup> Their assignment, however, of the indirect gap to  $H_5 \rightarrow A_6$  (double-group notation) may not be entirely correct since the KKR band structures did not include the  $M$  point of the Brillouin zone.

We turn now to examine the pressure dependence of the electronic density of states. In the top of Fig. 2, we show the 0-kbar theoretical (solid line) and experimental photoemission<sup>29</sup> (dashed line) results. The agreement is excellent. At the bottom of Fig. 2 we show the theoretical results at 8 kbar. The effects of pressure, although small, clearly result in a broadening of all the bands. This is caused by the increase in overlap between the wave functions on different chains.

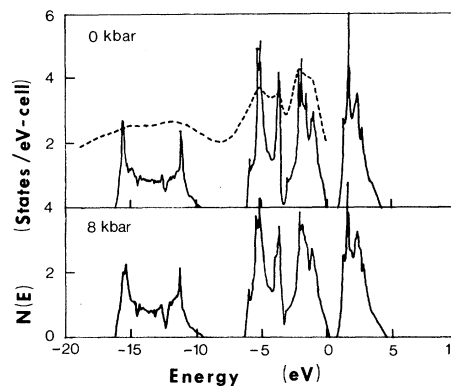


FIG. 2. Top: Theoretical density of states (solid line) and experimental photoemission measurements (dashed line, Ref. 29) at 0 kbar. Bottom: Theoretical density of states at 8 kbar. The empty conduction band is shown at positive energies.

This then also accounts for the shift of reflectivity peaks and absorption edge to lower energy with pressure. This change in wave functions, of course, also affects the optical matrix elements. To obtain a measure of this, we can write the frequency-dependent imaginary part of the dielectric function as a product of an average frequency-dependent matrix element and associated joint density of states.<sup>30</sup> Although the associated joint density of states increases uniformly with pressure, we find that the largest changes are brought about by the average matrix element.

In summary, we have introduced a simple yet accurate theoretical formalism which is nearly first-principles and contains the average effects of final-state relaxations. In applying this theory to the electronic structure of Se, we have shown that the optical properties can be explained without appealing to microscopic-field effects and that the pressure dependence of the optical properties arises from the increased coupling between chains which broadens the bands and enhances the matrix elements. Local fields are most prominent for systems with very localized charge distributions. Under pressure, the dielectric response for these systems would exhibit an increase beyond that expected from mere volume changes. This would arise because of the pressure-induced changes in the local fields. One would not, however, expect the polarizability of the very localized electronic states to change. In Se, on the other hand, although the electrons are localized in chains, their wave functions have nonnegligible overlap between neighboring chains. Under pressure, the dielectric response is increased

beyond that caused by normal volume changes because of the increased overlap. This overlap results in a change of the electronic polarizability and an enhancement of the dielectric response. Our results, therefore, show that local fields are not necessary to explain this enhancement. Furthermore, since microscopic-field effects are apparently small, the broad features in the spectra of the optical properties can provide direct information about chemical bonding not only in Se but in the wider range of materials closely related to it.

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## Spin Polarization of Field-Emitted Electrons and Magnetism at the (100) Surface of Ni

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The electron spin polarization of field-emitted electrons from atomically clean, field-evaporated in ultrahigh vacuum, single-crystal Ni tips has been measured with the probe hole selecting emission from the high-work-function (100) plane. We find  $P = (-3.0 \pm 1)\%$  (magnetic moment antiparallel to the magnetization of the crystal). From an analysis of these and recent photoemission data we conclude that the magnetic (and electronic) properties of the surface and bulk Ni must be very similar.

Electron spin polarization (ESP) measurements in photoemission<sup>1</sup> from Ni single crystals have revealed negative ESP at threshold. At photothreshold, many-body effects of the type pro-

posed by Anderson<sup>2</sup> and others<sup>3</sup> are not operative, and furthermore, because of the large escape depth of the low-kinetic-energy electrons, photoemission tests primarily bulk properties. Con-