

ELECTRONIC SPECTRUM, k CONSERVATION, AND PHOTOEMISSION
IN AMORPHOUS GERMANIUM

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The electronic energy spectrum of amorphous Ge is computed. Energy distributions of photoemitted electrons are determined, and the results are in excellent accord with experiment. Our analysis shows that the short-range order is primarily responsible for the observed spectral structure. Long-range disorder, however, has a strongly perturbing influence on some of the spectra. It appears that there is little difference between the valence-band density of states in the amorphous and crystalline forms, but increased disordering can cause a red shift of the $\epsilon_2(\omega)$ peak.

Donovan and Spicer have recently investigated the photoemission¹ and optical-reflectance spectra² of amorphous germanium films. They find considerable changes in the overall spectra with respect to crystalline Ge, although the density of states appears to retain sharp edges corresponding to the valence- and conduction-band extrema. This immediately raises the question as to how much information one needs in order to predict the experimentally observed spectra. Indeed, is the electronic structure determined primarily by a local crystalline ordering, or should we think of it as arising from a random arrangement of germanium atoms? A concomitant question is the relevance of crystal momentum (\vec{k}). Donovan and Spicer analyzed their data in terms of non-direct transitions which is tantamount to assuming that \vec{k} is completely nonconserved in optical transitions.

In this Letter we will show that the gross features of the density of states can be related to strong (umklapp) scattering effects associated with the short-range order in the disordered phase. In particular, crystal momentum, although a poorly defined quantity, still has relevance. In order to demonstrate these ideas in a quantitative way, our study must necessarily take explicit account of the lack of long-range order. This considerably perturbs the spectra of the amorphous solid. The disorder is introduced as a scattering background whose strength is roughly inversely proportional to the magnitude of the short-range order parameter. We will be able to give a very good accounting of both the photoemission curves and the $\epsilon_2(\omega)$ data. We also show that the nondirect model can be expected to give fairly good results for the photoemission spectra but places the valence-band density of states too close to the forbidden gap (by ~ 1.5 eV). The presence of quasi crystal selection rules and umklapp-enhanced optical transitions is most

evident in the $\epsilon_2(\omega)$ data.

It is known from diffraction studies^{3,4} that in the amorphous Ge phase the first- and second-neighbor coordination number is the same as in the Ge crystal. Furthermore, the bonding length is unchanged to within a percent or so. On this basis alone, we could think of the ordering as characteristic of either the diamond or wurtzite structure. Actually the electronic energy bands are expected to be remarkably similar for these two crystal forms,^{5,6} supporting the theme of this Letter, namely, that there is sufficient short-range order present to determine the gross features of the electronic spectrum. Furthermore, the strong broadening effects (~ 1 eV) induced by the disorder scattering described below are sufficient to wash out most of the small differences between the two. We will take the diamond form as our starting point, however, as annealing of amorphous Ge film gradually converts it to the diamond modification.

We then expect there to be present in the Hamiltonian a term which strongly couples plane waves whose number difference $\vec{K}_i - \vec{K}_j$ is equal to a reciprocal lattice vector. This is similar to the umklapp scattering found in the perfect crystal. Since the bonding length is unchanged, the umklapp scattering, of course, occurs at the same wave numbers as for the crystal. If the bonding length were to vary, then the strong coupling would occur at wave numbers other than those of the crystal. This in turn would lead to considerable changes in the observed energy gaps. This follows since the gaps depend on the pseudopotential coefficients $V(\vec{K})$ which are strongly dependent on the magnitude of K . These large gap changes have been noted by Herman in a previous work.⁸

We take the atomic pseudopotential in the amorphous solid to be identical to that of the crystalline solid. This is suggested since the Ge bonds

are completed (four near neighbors), and the bonding length is unaltered. Experimental studies do seem to indicate an increase of atomic volume in the range 0-15%,^{1,8} presumably due to bond twisting. Such a volume dilation implies a corresponding reduction in the pseudopotential form factor as used in the actual band calculation. This is due to the increase in atomic volume which enters a normalization factor in the pseudopotential approach (fewer atoms per unit volume). We have taken a modest 9% increase in atomic volume and corresponding 9% decrease in the effective pseudopotential. This causes level shifts of at most $\sim \frac{1}{3}$ eV for the most sensitive levels. Complete band structure has been calculated and the results presented elsewhere.⁹ Our energy gap in the disordered phase is reduced by ~ 0.3 eV compared with the crystalline energy gap. The experimental shift is ~ 0.15 eV which indicates that 5% would be a better choice for the atomic-volume expansion. Further experimentation will undoubtedly settle this question.

Before making comparison with experiment, we must account for the long-range disorder. As in our previous study, we assume that the principal effect is to produce elastic electron-lattice scattering whose rate is governed by the density of final scattering states, i.e.,

$$|\langle \psi_{nk} | H_{\text{scatt}} | \psi_{n'k'} \rangle|^2 = M^2, \quad (1)$$

where M^2 is treated as an adjustable constant. We can then proceed at once to a calculation of the amorphous density of states in terms of the crystal density of states:

$$N_{e,h}(\epsilon_f) = \int N_{e,h}^0(\epsilon_k) A_{e,h}(\epsilon_k, \epsilon_f) d\epsilon_k. \quad (2)$$

The same momentum-independent approximation to the spectral weight function ($A_{e,h}$) made in Ref. 9 has been employed. Here $N_{e,h}(\epsilon_f)$ is the amorphous density of states, and $N_{e,h}^0(\epsilon_k)$ is the crystalline density of states. ϵ_f is measured from the valence-band edge for both electrons (e) or holes (h). The matrix element, M^2 , was chosen previously so as to give agreement with $\epsilon_2(\omega)$, and is the only adjustable parameter in this study. It was found to be 12 times greater than the scattering rate due to optical and acoustic phonons in the perfect crystal. This suggests a short-range order parameter ~ 10 -20 Å, and in turn that the wave-number uncertainty is about $\frac{1}{4}$ of the cell dimension.¹⁰

The computed density of states for amorphous Ge is shown in Fig. 1. We note that the first big peak in $N_h(\epsilon_f)$ is centered about the X_4 level in

the valence band while the peak near -7 eV on the diagram is associated with the X_1 states. These peaks are so intense in the crystal that they persist into the amorphous phase, and bear dramatic witness to the importance of the quasi-zone boundaries. The conduction-band structure is too weak to survive disordering significantly. The three small peaks which are seen in Fig. 1 near 1.5, 3.5, and 4.5 eV are seen quite prominently as sharp structures before the background scattering is introduced. The first of these is correlated with the K points and Σ directions. The second can be associated with the L_3 conduction-band states. We have not traced the third to any particular group of states and it is presumably a volume effect.

Note that the energy separation between the big peak in the valence bands and the plateau in the conduction bands is close to 4 eV. This is in contrast to the experimental² and theoretical peak position (Fig. 2) of ~ 2.6 eV in $\epsilon_2(\omega)$. We clearly see that a nondirect model would fail to explain the optical absorption in terms of the amorphous density of states since this makes the probability of transition simply proportional to the combined density of initial and final states. Our explanation of the peak position is fairly simple. We remember that in the crystal the oscillator strength of transitions near the forbidden gap are strongly umklapp enhanced. Disorder smears out the optical structure but leaves the red end of the spectrum much more intense than the blue. Thus the short-range order is sharply manifested in the behavior of $\epsilon_2(\omega)$ via the oscillator strength. Our model also predicts a blue shift of the $\epsilon_2(\omega)$ peak with a decrease in disorder (until the crystalline spectrum emerges). This is due to an average shift toward the red of oscillator strength with increasing disorder.

The photoemission energy distribution curves (EDC's) provide probably the best test of these

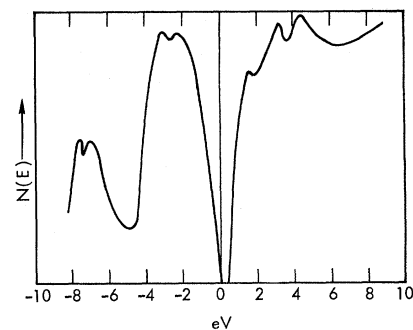


FIG. 1. Density of states of amorphous germanium.

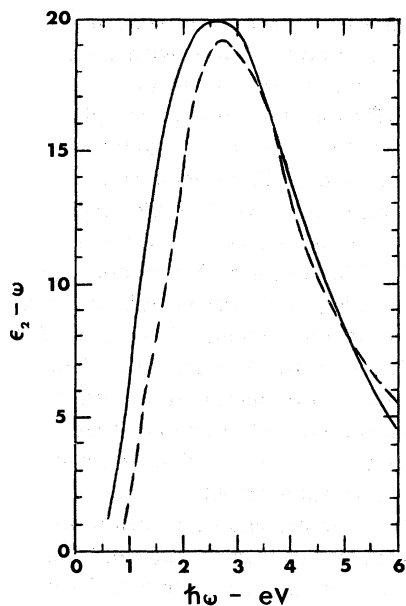


FIG. 2. Comparison of the theoretical calculation of $\epsilon_2(\omega)$ (solid line) with the experiment of Donovan, Spicer, and Bennett (dashed line).

density-of-states ideas. In Fig. 3 we show the EDC's. The curves are given for several values of $\hbar\omega$, and in order to get a reasonable shape, we have modified the internal distributions by a free-electron escape function. In addition to the results as derived using spectral weight ideas, we have computed EDC's in terms of Spicer's nondirect model. Although the spectral weight approach explicitly retains dipole matrix-element effects and partial k conservation, Fig. 3 clearly shows that the EDC's as deduced by the two models are remarkably close. This is in part due to the fact that in the far ultraviolet the matrix can be reasonably well approximated by a constant. The effects of direct transitions are smeared out by the scattering background. Note that a non-direct argument working backward to the density of states places the valence-band peak too close to the forbidden gap. The primary reason for this is that the escape function shifts the photoemission peaks toward the high-energy end. The curves presented in Fig. 3 agree remarkably well with the experimental data.¹

In conclusion, we believe that the present discussion shows conclusively that the continuum electronic spectrum of amorphous Ge is primari-

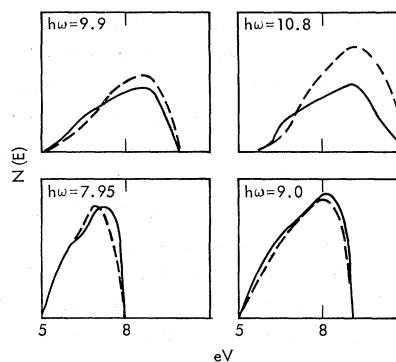


FIG. 3. The spectrum of photoemitted electrons from amorphous Ge as computed entirely within the spectral-weight framework (solid line) and applying the nondirect model to the computed density of states (dashed line). All the curves have been corrected by use of a free-electron escape function. No normalization of the curves has been made, and no significance should be attached to the vertical scale in comparing different plots.

ly due to the short-range geometrical ordering of the atoms. It is interesting to note that liquid Ge is metallic.¹¹

The change in conductivity is apparently due to an increase of coordination number in the liquid phase demonstrating an alteration of the short-range order.

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