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Similarities in the Valence Bands of Amorphous and Crystalline GeTe Determined by X-Ray Photoemission

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We have measured the valence-band density of states and the energies of the core levels of crystalline and amorphous GeTe with x-ray photoemission. The density of states of the amorphous form is found to be very similar to that of the crystal. The present results indicate that the atomic orbitals primarily determine the valence-band density of states and that these are disturbed little, even when the bonding changes significantly.

Although the details of the structure of amorphous GeTe have not been conclusively determined, it is well established that the amorphous and crystalline phases are significantly different.[1-5] The density of the amorphous form has been measured to be 5.6 ± 0.5 g/cm^3, compared with the crystalline density of 6.17 g/cm^3.[6,7] In the crystalline form, GeTe has a slightly distorted rocksalt structure in which each atom is coordinated to six neighbors of the opposite kind with a separation of 3.0 Å. In the amorphous form the coordination number is reduced to an average of about 3, with a nearest-neighbor separation of 2.7 Å.[1-5] Thus, in the amorphous form not only is the long-range order absent, but the short-range order is very different from that of the crystal. The structural data of the amorphous form are best described by a random covalent model in which Ge-Ge, Te-Te, and Ge-Te bonds are equally likely, while Ge remains fourfold coordinated and Te twofold coordinated.[3]

The change in the structure was interpreted as representing a change in the bonding from ionic in the crystal to covalent in the amorphous form.[2] The change in the zero-frequency dielectric constant, from 36 in the crystalline form to 11 in the amorphous form,[8] indicated that large changes were taking place in the bonding. Brodsky and Stiles[8] suggested that the strengthening of the bonding in the amorphous form arose from the shortening of the interatomic distances, leading to a rescaling of the parameters E_h and C, which determine the features of the band structure. Even aside from the destruction of the long-range order, one would expect the large changes in these parameters alone to modify the valence-band density of states drastically.

Compounds which crystallize in the rock-salt structure are believed to do so because of the pronounced ionic character of their bonds. If the ionicity were indeed to increase by a large amount upon crystallization, then we should expect to see large shifts in the positions of the core levels of the Ge and Te atoms in opposite directions, due to the charge transfer between the two types of atoms. X-ray-induced electron emission is the ideal tool for such investigation because differences between core levels (e.g., Ge 3*d* and the $j = \frac{5}{2}$ component of the Te 4*d* orbitals) can be measured to within ±0.1 eV.[9] The determination of any change of this difference which would correspond to the charge transfer is particularly accurate. For comparison, such a shift is about 4.0 eV for the Te $4d\,\frac{5}{2}$ level due to the difference of valence electrons around the Te in the compounds PbTe and TeO.[10] If, on the other hand, the crystallization of GeTe were not accompanied by charge transfer (i.e., the character of the bond remains unchanged), then the core levels should not shift either.

Betts, Bienenstock, and Bates[11] reported that the Ge $3d$ levels in amorphous and crystalline GeTe differ by 2.8 eV in samples of an unspecified oxidation state, indicating a large increase of the ionic bonding character for the crystalline material.

Previous high-resolution uv photoemission measurements[12] have shown that differences exist in the top of the valence bands of the amorphous and crystalline forms. However, because, of the small photon energies used, information from more than 5 eV into the valence band was not obtained.

Here we present x-ray photoemission data on amorphous and crystalline GeTe films from which we have determined the valence-band electronic density-of-states curve, and the plasma frequencies. We show that, despite the large changes in the structure, the photoemission from the two forms is surprisingly similar.

The electron spectrometer which we used is a Vacuum Generators ESCA III instrument, with Al $K\alpha$ radiation of 1486.6 eV as the excitation source. The samples were dc sputtered at a rate of 1000 Å/h in a high-purity argon atmosphere at 20×10^{-3} Torr. The work of others[6,7] has shown that films deposited onto substrates held at less than 130°C are amorphous, while those deposited at higher substrate temperatures are crystalline. The amorphous and crystalline films, from which the data of Fig. 1 were taken, were deposited at substrate temperatures of 125 and 575°K, respectively.

The samples were transferred directly into the analyzing chamber without breaking vacuum. The vacuum in the analyzing chamber was better than 5×10^{-10} Torr. The x-ray photoemission spectra (XPS) showed no trace of contamination by oxygen or carbon within our limits of detection, which is estimated to be 3 atoms out of 100 in the participating surface layer. The work-function calibration of the spectrometer was made with the $4f\,\frac{7}{2}$ line of Au taken to have the value of 83.9 eV. The instrumental resolution for the core levels was 1.2 eV, and for the valence band, 1.5 eV. Simultaneous uv photoemission measurements, to be reported elsewhere, indicate clearly that the samples deposited at a substrate temperature of 125°K were amorphous, while those deposited at 575°K were indeed crystalline.[13,14]

Similarities in the raw photoemission data for the amorphous and crystalline phases can be seen in Fig. 1(a). Both curves rise with increasing binding energy because of the contribution from electrons inelastically scattered within the sample. Subtracting the inelastic electrons gives the density-of-states curves shown in Fig. 1(b). It is clearly seen that the densities of states are very similar. The first peaks of two forms overlap, but the lower two peaks in the amorphous form are broader than those of the crystal. The zero of the binding-energy scale is meant to coincide with the top of the valence band.

The valence band for the crystalline form shows the expected three-peak structure for materials of this kind. The peak of lowest binding energy between 0 and about 5 eV is certainly due to the

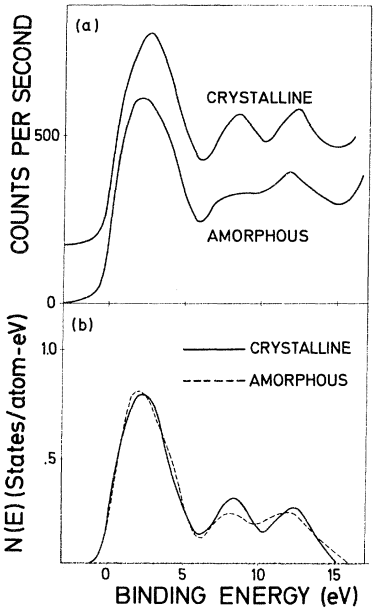

FIG. 1. Electron emission spectra of GeTe in the amorphous and crystalline forms. The curves for the amorphous GeTe have been shifted by 0.6 eV so that the onset of the valence band coincides with that of the crystalline form, which is used as reference point for the "binding energy" scale. (a) Experimentally obtained curves, (b) curves corrected with respect to the background of inelastically scattered electrons and normalized so that the total area corresponds to the number of valence electrons per atom.

Ge $4p$ and Te $5p$ orbitals. It is asymmetric (thus suggesting unresolved additional structure) and peaks at about 2.3 eV. The second maximum, which is due to the Ge $4s$ orbitals, peaks at about 8.3 eV, and the last, which is due to Te $5s$ electrons, peaks at about 12.4 eV. Tung and Cohen[15] have calculated the GeTe band structure using the empirical pseudopotential method. Estimating a density-of-states distribution from their band structure plot, one should expect the first, second, and third maxima to occur at 2.6, 7.2, and 16, respectively. Band-structure calculations which are in better agreement with our results have been carried out by Herman *et al.*[16] using a relativistic orthogonalized plane wave method. The respective maxima of their density of states distribution are estimated to occur at about 2.5, 8.0, and 12.0 eV.

Some slight differences appear nevertheless in Fig. 1(b) between the amorphous and the crystalline curves. The main peak, which occurs at 2.3 in the crystalline materials, is slightly shifted towards lower energies in the amorphous case. Also, the shoulder which appears at around 3.5 eV in the amorphous case is absent for the crystalline materials. This structure, plus an additional shoulder around 0.5 eV for the crystalline materials, is better resolved in uv photoemission work.[13,14] The ratio of the three peaks should be, in the absence of matrix element effects, 3:1:1. This is the approximate ratio observed in the corrected XPS curves. Although our instrumental resolution is 1.5 eV, the differences observed in the valence bands of the two forms, in light of the preceding discussions, are small.

The Ge $3d$ and Te $4d$ levels for the amorphous and crystalline forms are presented in Table I. The deeper core levels will be reported elsewhere.[13] Both the Ge and Te levels in the amorphous form were measured to have shifted on the average by 0.6 eV to higher binding with respect to their location in the crystalline form. This, most likely, indicates a shift in the Fermi level rather than a true increase in the binding energy.[6] There are no relative shifts between the Ge and Te levels to within ± 0.2 eV. Such small differences between the Ge and Te levels in the amorphous and crystalline forms indicates that there occurs no drastic charge redistribution around Ge and Te, and that the ionicity of the bond should be considered to remain unchanged. This is in contradiction to earlier results claiming a 2.8-eV shift.[11] (Shifts of this magnitude usually result from surface oxidation.) The sharpness of the core levels remains essentially the same for both structural forms within our resolution of 1.2 eV.[13]

TABLE I. Binding energy of germanium $3d$ and tellurium $4d$ levels in crystalline and amorphous GeTe samples (in eV with respect to the Fermi level in each sample). We have added, for comparison, values reported for elemental Ge and Te.

	Ge $3d$	Te $4d_{5/2}$	Te $4d_{3/2}$
Element	29.4[a]	40.31[b]	41.80[b]
c-GeTe	29.8	40.05	41.5
a-GeTe	30.3	40.6	42.1
$\Delta(a-c)$	+0.5	+0.55	+0.6

[a] Our measurements.

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The plasma frequencies of the valence bands as determined from loss spectrum following the $L_3M_{45}M_{45}'$ Ge Auger transition were measured to be 16.9 ± 0.3 and 16.4 ± 0.3 eV for the crystalline and amorphous forms, respectively. This difference is close to the one estimated solely from the known density change between the crystalline and amorphous forms.

Our work on the core levels of GeTe shows no evidence that the two modifications exhibit different electron configurations, or that upon crystallization of the amorphous material a substantial charge transfer takes place between Ge and Te valence electrons as postulated by earlier work. The observable change in the separation of Ge and Te core levels (<0.2 eV), is no larger than that corresponding to the ionicity difference between HgTe and CdTe.[9]

Secondly, we have shown that the valence-band densities of states of the two modifications of GeTe, as measured with XPS, are similar, i.e., the spectrum of the amorphous GeTe can be interpreted as a broadened version of that of crystalline GeTe. On the other hand, there is no reason to doubt that during this phase transition, not only the long-range order but also the short-range order has changed, as evidenced by the changes in the dielectric constant, radial distribution functions, and density.

One may speculate that, because of the relatively small electronegativity differences between the Ge and Te atoms,[17] the energies of their atomic orbital states are not drastically influenced by the type of atoms surrounding them. Thus, to first order one may approximate the valence-band electron density of states of amorphous GeTe as a sum of those of amorphous Ge and of amorphous Te.[13] Such a model is based on the structural similarity to amorphous GeTe containing amorphous Ge-like and amorphous Te-like bonds. It is found that the *s* levels of this model are broader than those observed.[13] This can be explained by the presence of Ge-Te bonds in amorphous GeTe. Any tendencies to bring *s* orbitals lying at different energies together tends to weaken the resonant bonding, thereby making the levels sharper.

However, the similarities in the XPS of the amorphous and crystalline forms suggests that also the density of states of the crystalline form can serve as an adequate first approximation for the density of states of the amorphous form. The crystalline form is structurally unlike the amorphous form and application of such a model is not by any means *a priori* obvious. Neverthless, we can explain the broadening of the *s* levels in the amorphous form by tendencies of like atoms to be nearest neighbors.

We conclude that valence bands of amorphous and crystalline GeTe are similar even though their structures are significantly different. This suggests that within the resolution of nonmonochromatized electron spectroscopy for chemical analysis (~ 1.5 eV), the density of valence states of a given compound is essentially unaffected by changes in the long- and short-range order.

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Spin-Flop Domains in MnF_2†

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An intermediate state is shown to exist between the antiferromagnetic and spin-flop states of antiferromagnetic MnF_2. This state consists of alternate thin-slab domains of antiferromagnetic and spin-flop material. Experimental evidence includes NMR, Faraday rotation, optical-absorption spectroscopy, and photographs of the domain structure. A molecular field model is used to calculate the field width of the domain region and the physical width of the domains. Reasonable numerical agreement is found.

In studying the F^{19} NMR near the spin-flop (SF) transition in antiferromagnetic MnF_2, evidence was found for a new type of intermediate state between the antiferromagnetic (AF) and SF states. In a narrow region of magnetic field (≈ 1 kG) near SF, the NMR frequency is completely indepen-