Evidence for Covalent Bonding in Crystalline and Amorphous As, Sb, and Bi from Valence-Band Photoelectron Spectra[*]

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X-ray photoelectron spectra (XPS) of the valence bands of crystalline and amorphous As, Sb, and Bi have been measured. The results are compared with band-structure calculations for the crystalline materials. A splitting, ΔE, of the "s-like" peak for the crystalline phase disappears in the amorphous phase and the "p-like" peak is shifted towards higher energies. This similarity to tetrahedrally coordinated covalent semiconductors is explained by describing the semimetals as layers of distorted covalently bonded hexagonal rings. This generalizes the "even-odd" ring effect previously observed in group-IV semiconductors to the $A7$ lattice of As, Sb, and Bi. The relation of ΔE to the interatomic distance is described by a universal curve, which applies to the group-V semimetals as well as group-IV semiconductors.

I. INTRODUCTION

Weaire and Thorpe have used the concept of topological disorder in attempting to understand the properties of amorphous semiconductors.[1-8] They used model Hamiltonians of the tight-binding type to calculate the density of states in crystals of the diamond structure, and obtained the characteristic splitting in the lowest "s-like" peaks in the valence bands using these Hamiltonians. They emphasized the importance of six-membered rings in the diamond structure and suggested that a random-network amorphous structure, with both fivefold and sixfold rings, would not exhibit well-resolved splitting in the s-like peak. Joannopoulos and Cohen carried out empirical-pseudopotential-model (EPM) band-structure calculations on several forms of silicon and germanium.[4] They found a single broad s-like peak in $\rho(E)$ for the ST-12 structure, which has five- and seven-membered rings, and they attributed the lack of splitting to the presence of odd-numbered rings. Single s-like peaks were indeed observed in the x-ray photoelectron spectra (XPS) of amorphous silicon and germanium.[5] Both the form of Weaire and Thorpe's one-band Hamiltonian and the discussion by Joannopoulos and Cohen may be interpreted as implying splitting in the s-like peak in a broader context than the diamond lattice, and loss of this splitting in the amorphous state. We report XPS on crystalline and amorphous As, Sb, and Bi which show exactly this behavior. Furthermore, for the six elements studied to date, the s-peak splitting falls on a universal curve when plotted against nearest-neighbor distance. Thus both s-peak splitting in the crystalline state and its disappearance in the amorphous state appear to be general phenomena for simple covalent solids. In addition to its intrinsic theoretical importance, this result should prove valuable both as a diagnostic device for identifying amorphous phases and as a covalent reference point for establishing an ionicity scale.

II. EXPERIMENTAL

The XPS measurements were performed in a Hewlett-Packard 5950A ESCA spectrometer using monochromatic AlK_α x rays. The over-all resolution of this instrument as determined from the broadening of the Fermi edge in the valence-electron density of states of several metals[6] was 0.55 eV.

Monocrystalline samples of As, Sb, and Bi were cleaved in a dry N_2 atmosphere and immediately transferred into the spectrometer vacuum without exposure to air. No oxygen contamination was detected by *in situ* monitoring of the O 1s line on the As sample. Small amounts of oxygen on the Sb and Bi samples could easily be removed by gentle (200 eV, 10 μA) argon-ion bombardment for 45 sec and 2 min, respectively. During the measurements a pressure of 5×10^{-8} Torr was maintained, and no oxygen or carbon buildup was observed. The accumulation time for each spectrum varied in the range from 6 to 10 h.

Amorphous As was prepared in the spectrometer by flash evaporation of a thin film onto a gold substrate at room temperature. The amorphous Sb and Bi samples were prepared by argon-bombarding single-crystal surfaces for about 30 min with 10 μA of 900-eV Ar$^+$ ions. Earlier experiments[5] with Si and Ge yielded essentially identical "amorphous" spectra for evaporated films and argon-bombarded crystals.

III. RESULTS AND DISCUSSION

The uncorrected photoelectron spectra $I(E)$ of the valence-band regions of the crystalline and amorphous modifications of the three semimetals are
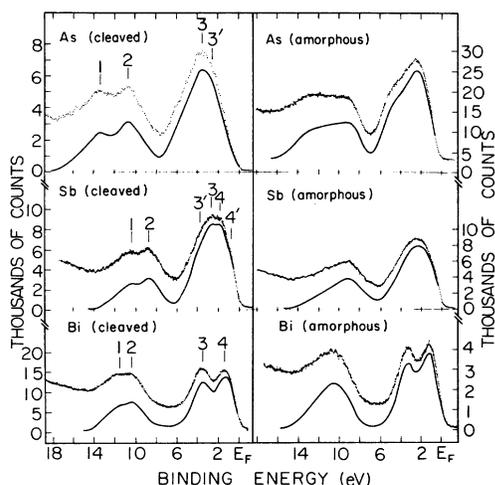
FIG. 1. Uncorrected (dots) and corrected (line) photo-electron spectra of the crystalline and amorphous semi-metals.

shown in Fig. 1, together with the corresponding corrected spectra $I'(E)$. A response function was constructed from the low-energy tails of the nearby d levels (not shown) in each case to correct for secondary electrons in $I(E)$. In an iterative unfold-ing procedure, using these response functions, the corrected spectra $I'(E)$ were obtained.

The over-all similarity of the XPS in Fig. 1 re-flects the similarities of electronic configuration $(s^2 p^3)$ and, for the crystalline samples, of crystal structure ($A7$ in each case) in these group-V ele-ments. There are two atoms per unit cell in the $A7$ structure, with ten electrons filling five valence bands. In free atoms of these elements, the va-lence s electrons are bound 8–10 eV more tightly than the valence p electrons. The mean splittings between peaks 1-2 (Fig. 1) and peaks 3-4 (Fig. 1) are approximately 8.4 eV (As), 7.2 eV (Sb), and 8.6 eV (Bi). Using the free-atom configuration

$s^2 p^2_{1/2} p_{3/2}$, the mean s-p splittings in free atoms[7] can be estimated as 9.8 eV (As), 8.4 eV (Sb), and 9.7 eV (Bi). Since the cohesive energies of these elements[8] are only 2–4 eV per atom, one would ex-pect $a priori$ to find separate peaks corresponding to s and p electrons, in the absence of unusually strong s-p mixing, with the s peak(s) lying lower. Theoretical band-structure calculations do indeed show two reasonably well-separated s-like bands several eV below the Fermi level E_F, and three p-like bands near E_F.[9-11] We assign the lower peak (labeled 1-2 in Fig. 1) to the former and the upper peak (3-4 in Fig. 1) to the latter. Derived energies of characteristic features in $I'(E)$ for the crystalline samples are set out in Table I together with the binding energies of the outermost d elec-trons. Although the same two general features were observed in the spectra of the amorphous ma-terials, most of the finer structure was completely lost.

It has been shown in recent investigations of the valence-electron spectra of elements[5] and simple binary compounds[12] that the interpretation of photo-emission data in terms of the density of states $\rho(E)$ of the solid is quite justified, provided effects of photoelectric cross-section variation throughout the valence bands are properly taken into account.[13] Densities of states provide therefore the best means of a detailed and quantitative comparison of photo-electron spectra with theoretical band structures and experimental data related directly to the band structures. Several band-structure calculations for the semimetals As, Sb, and Bi (Refs. 9–11) have been carried out along various symmetry di-rections in the Brillouin zone, but they all lack the detailed mapping of energy levels throughout an ir-reducible part of the Brillouin zone which is nec-essary to derive $\rho(E)$. A comparison of these cal-culations with our measurements is therefore lim-ited to some prominent features which can easily

TABLE I. Binding energies of characteristic features in the XPS of crystalline As, Sb, and Bi.

As (eV)		Sb (eV)		Bi (eV)	
Bottom of valence band	17.0 ± 0.3	Bottom of valence band	13.3 ± 0.3	Bottom of valence band	14.0 ± 0.2
1	13.26 ± 0.10	1	10.45 ± 0.08	1	11.54 ± 0.10
2	10.64 ± 0.08	2	8.78 ± 0.06	2	10.36 ± 0.08
3	3.53 ± 0.06	3'	3.68 ± 0.20	3	3.45 ± 0.05
3'	2.51 ± 0.13	3	2.63 ± 0.09	4	1.30 ± 0.06
E_F	0.0 ± 0.05	4	1.87 ± 0.08	E_F	0.0 ± 0.05
		4'	0.82 ± 0.06		
		E_F	0.0 ± 0.05		
$3d$	41.7 ± 0.1	$4d_{3/2}$	33.44 ± 0.09	$5d_{3/2}$	26.94 ± 0.07
		$4d_{5/2}$	32.14 ± 0.09	$5d_{5/2}$	23.90 ± 0.07

be deduced from an inspection of the given band structures.

Relatively flat parts of the p-like bands between symmetry points Γ and L and along the Γ-T direction near the Fermi level can most likely be identified with the maxima 3-3′, and 3-4 in the density of states of As and Sb, respectively. The band minima of these bands at points U, X, and W and the Fermi level mark bottom and top of these peaks.

The mean positions of the lower doublets 1-2 in the photoelectron spectra are approximately determined by the energy of the two s bands at L_1, L_4, and X_4 while the width is unambiguously given by the separation of these two bands at point Γ in the center of the Brillouin zone. At this level of interpretation we compare in Table II available band-structure calculations of the semimetals with the photoelectron spectra of the crystalline species. The agreement for As and Sb is as good as can be expected, except for the total width of the valence bands, which is consistently calculated too small, the difference decreasing from 3 eV in As to 1 eV in Sb. Augmented-plane-wave (APW)[11(a)] and EPM[11(b)] band-structure calculations for Bi both underestimate the width of s and p bands by considerable amounts: 1.7 eV (APW) and 1.9 eV (EPM) for the s bands, and 0.8 eV (APW) and 1.5 eV (EPM) for the p bands.

Moreover, the EPM calculation yields a mean separation of the s and p valence bands which is about 2 eV smaller than our experimental result. The reason for this discrepancy may be found in the final adjustment of the pseudopotential parameter A [Ref. 11(b)], which summarizes the effects of relativistic corrections and the nonlocal character of the pseudopotential on bands with s-atomic character.

Moving down from As to Bi, changes in the structure of the p-like peak arise dominantly from relativistic effects rather than from crystal-field effects. The single asymmetric peak 3 in As splits into two peaks (3 and 4) in Sb. The splitting increases to 2.2 eV in Bi. It has been shown for Bi[14] that this splitting can be identified with the effect of spin-orbit interaction on the p-like bands near the center of the Brillouin zone (Γ). The relativistic Hartree-Fock-Slater free-atom value[7] of 2.16 eV for the $6p$ spin-orbit splitting in Bi corresponds closely to the observed splitting in the p-like band. The measured value for Sb of 0.76(8) eV compares equally well with the calculated $5p$ free-atom value of 0.71 eV. It is unusual for the spin-orbit splitting to come through so cleanly as a splitting in the valence-band density of states, because the Hamiltonians for the spin-orbit and crystal-field interactions do not commute and the corresponding energies are not additive. The d bands of silver[6] and gold[15] provide counterexamples in which the split-

ting far exceeds the free-atom spin-orbit splitting in magnitude. Shoulders 3′ and 4′ in the $I'(E)$ curve for Sb most likely arise from bands near the symmetry points L_4 and T_1 and X_3 and X_4 in the Brillouin zone.

Turning now to the s-like bands, we observe a pronounced splitting of the s peak (1-2 in Fig. 1) in the densities of states of all three group-V semimetals As, Sb, and Bi. This splitting decreases from 2.62(8) eV in As to 1.67(6) eV in Sb to 1.18(8) eV in Bi (see Table II). A parallel decrease in width (full width at half-maximum) of this peak from 5.2(2) to 4.6(2) to 4.0(1) eV is also evident. The two components of the s peak differ in intensity in each case. After decomposition into two peaks, we obtain an intensity ratio of 1.3 for As, 1.3 for Sb, and 1.2 for Bi. Since only two nondegenerate bands are responsible for the doublet structure, this intensity difference is most likely due to cross-section modulation of the photoelectric effect. An admixture of p-like character into band 2 would increase its photoelectron cross section relative to that of band 1 as was earlier observed for Ge.[5] In Bi the drop in the intensity ratio coincides with a marked increase in the mean s-p band separation because of the relativistic lowering of the s-electron energy. This provides direct experimental evidence for the dehybridizing effect of relativistic corrections in solids.

The density-of-states results for amorphous As, Sb, and Bi are significantly different from those of the respective crystalline modifications. The s bands do not exhibit double-peaked structure and there is less structure in the p-like bands in As and Sb, while the spin-orbit splitting in Bi is unchanged. In all three cases the maximum in the density of states is shifted toward the Fermi energy by a few tenths of an electron volt. The replacement of peaks 1 and 2 in the crystalline samples by a single peak in the amorphous spectra is caused by a redistribution in the density of states rather than simply by broadening of the two peaks. This is especially true in Sb and Bi. As evidence for this we note that the total widths of the s-band peaks as well as the valley between the s and p bands remain essentially the same in going from the crystalline to the amorphous material.

The startling agreement between these observations and those made earlier[5] for the prototypical covalent crystals Si and Ge suggests an interpretation of the semimetal spectra along similar lines. The distortions which lead from the diamond fcc lattice to the $A7$ lattice of As, Sb, and Bi obviously do not destroy the main features in the density of states. The experimental s-band splitting in the semimetals is rather well reproduced by the separation of these bands at points T_1 and T_2' in the Brillouin zone, as shown by a comparison with avail-

TABLE II. Comparison of band-structure calculations with prominent features in the photoelectron spectra of As, Sb, and Bi. The theoretical entries are the position of the symmetry points listed in the last column. All energies are in eV.

Experiment (As)		Theory (As)			
	Binding energy	TB[a] Ref. 9b	EPM[b] Ref. 9(a)	SCF OPW[c] Ref. 9(b)	Symmetry points
E_F	0.0	0.7	0.8	0.9	
Peak 3'	2.5	2.1	2.4	2.2	T_3'
Peak 3	3.5	3.5±0.2	3.5±0.2[b]	3.5±0.2[d]	L_2, L_4, Γ_1
Bottom of peak 3	7.3	6.9	7.4	7.1	X_1
Mean position doublet 1, 2	11.8	11.5±0.4	11.6±0.4	11.5±0.4	L_1, L_4
Bottom of valence band	17.0	14.9	14.7	14.7	Γ_1
Splitting 1-2	2.62±0.08	2.90	2.83	3.27	$T_2' - T_1$

Experiment (Sb)		Theory (Sb)	
	Binding energy	EPM Ref. 10	Symmetry points
E_F	0.0	1.0	
Mean position of peak 3, 4	2.4	2.4±0.1	Γ_1, Γ_3, L_4
Bottom of peak 3, 4	5.5	5.8	X_1
Top of doublet 1, 2	7.0	7.1	Γ_2'
Mean position of doublet 1, 2	9.8	10.8±0.3	L_1, L_4
Bottom of valence band	13.3	13.1	Γ_1
Splitting of doublet 1-2	1.67±0.06	1.71	$T_2' - T_1$

Experiment (Bi)		Theory (Bi)		
	Binding energy	APW[e] Ref. 11(a)	EPM Ref. 11(b)	Symmetry points
E_F	0	0±0.2	0	
Bottom of doublet 3, 4	5.2	4.4	3.7	X_5
Top of doublet 1, 2	8.1	8.8	6.6	Γ_6^-
Mean position of doublet 1, 2	11.2	11.0±0.2	8.8±0.2	L_5, L_7
Bottom of valence band	14.0	13.0	10.5	Γ_6^+
Splitting of doublet 1-2	1.18±0.08	1.29	1.78	$T_2' - T_1$

[a]Tight-binding calculation.
[b]Empirical pseudopotential model; the results of potential "P1" are given.
[c]Self-consistent orthogonal-plane-wave calculation.
[d]Average energy and maximum deviation in the position of the symmetry points.
[e]Augmented-plane-wave calculation.

able theoretical data in Table II. Points T_1 and T_2' correspond to points L_1 and L_2' in the diamond lattice. It has been pointed out that the existence of sixfold rings in the diamond structure is crucial for the preservation of well-separated s bands (peaks 1 and 2) in the density of valence-band states which correspond to the bonding and antibonding s levels of covalently bonded atoms.[3,4] In As, Sb, and Bi the lattice is composed of layers normal to the trigonal axis. There are three weak bonds per atom between layers, and within a layer there are three stronger bonds which produce a two-dimen-

sional array of distorted hexagonal rings.[16] We therefore interpret the XPS of As, Sb, and Bi as extending the generality of the "odd-even" ring effect on the valence bands. Apparently s-peak splitting is present in these covalently bonded $A7$ lattice crystals because of the even-numbered rings, while the odd-numbered rings that presumably are present in the amorphous materials preclude resolution of these peaks into two simple components.

The "blue shift" of the p peaks in the density of the amorphous state gives a direct measure of the deviation of the sample from its ground equilibrium state. Joannopoulos and Cohen[4] have given an explanation for a similar effect in Si and Ge, which can readily be applied to the semimetals. The energy of electrons localized in the bond region between the atoms is sensitive to variations in bond angle through the repulsive Coulomb interaction between electrons in adjacent bonds. Though a decrease of one angle is always accompanied by an increase in another angle, the nonlinear interaction between the bonds results in a net increase in energy. This increase in energy is responsible for the blueshift of the p bands, which localize electrons primarily in the bond region. The lower s-like electrons are not affected by variations in bond angle because they are primarily localized on the atoms.

In this sense it is justified to refer to the two lower peaks in the density of states of covalently bonded elements as "s peaks" as distinguished from the "p peak" even though the symmetry of the two lowest *bands* may vary and may even be p like as is the case for the group-IV elements at point Γ'_{15} in the Brillouin zone. This point of view is consistent with the observed cross sections for x-ray photoemission from diamond, silicon, and germanium.[13]

Finally, the observed splitting in the two lowest valence-band peaks of the covalent groups-IV and -V elements C (diamond), Si, Ge, As, Sb, and Bi are related in a very simple way. When plotted against nearest-neighbor distance d, these splittings follow a universal curve given by
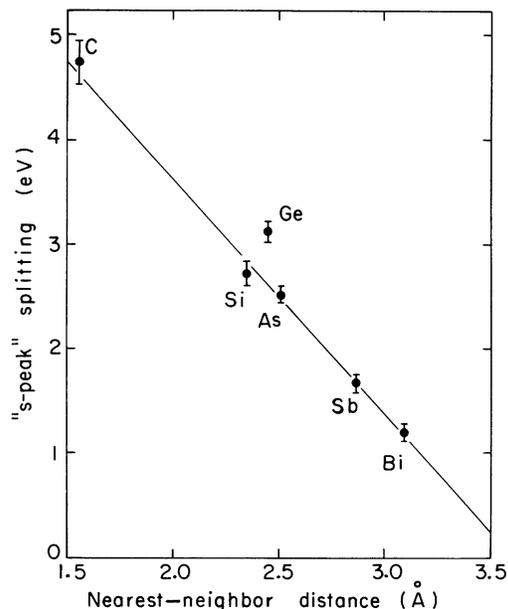
FIG. 2. Plot of the s-peak splitting vs the nearest-neighbor distance for covalently bonded elements; the carbon point (diamond) is taken from Ref. 13.

$$\Delta E(\text{eV}) = 8.0 - 2.2 \times d(\text{Å}) \ ,$$

as shown in Fig. 2. That ΔE should follow such a simple equation is somewhat surprising, because differences in coordination and hybridization might be expected to play a larger role. Apparently the effect of overlap, which of course decreases strongly with distance, is dominant. With further study it may be feasible to give a detailed explanation for the variation of ΔE. Meanwhile the observed ΔE-vs-d relation can serve as a covalent reference point in establishing an experimental ionicity scale based on valence-band spectra.

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[1]D. Weaire and M. F. Thorpe, Phys. Rev. B **4**, 2508 (1971).

[2]M. F. Thorpe and D. Weaire (unpublished).

[3]D. Weaire and M. F. Thorpe, in *Computational Methods for Large Molecules and Localized States in Solids*, edited by F. Hermann, A. D. McLean, and R. K. Nesbet (Plenum, New York, 1972).

[4]J. D. Joannopoulos and M. L. Cohen, Phys. Rev. B **7**,

2644 (1973).

[5]L. Ley, S. Kowalczyk, R. A. Pollak, and D. A. Shirley, Phys. Rev. Letters **29**, 1088 (1972).

[6]R. A. Pollak, S. Kowalczyk, L. Ley, and D. A. Shirley, Phys. Rev. Letters **29**, 274 (1972).

[7]C. C. Lu, T. A. Carlson, F. B. Malik, T. C. Tucker, and C. W. Nestor, Jr., Atomic Data **3**, 1 (1971).

[8]C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1956), p. 78.

[9](a) L. M. Falicov and S. Golin, Phys. Rev. **137**, A871 (1965); (b) S. Golin, Phys. Rev. **140**, A993 (1965).

[10]L. M. Falicov and P. J. Lin, Phys. Rev. **141**, 562 (1966).

[11](a) L. G. Ferreira, J. Chem. Phys. Solids 28, 1891 (1967); (b) S. Golin, Phys. Rev. 166, 643 (1968); (c) S. Mase, J. Phys. Soc. Japan 13, 434 (1958); J. Phys. Soc. Japan 14, 584 (1959).

[12]R. A. Pollak, L. Ley, S. Kowalczyk, and D. A. Shirley, Phys. Rev. Letters 29, 1103 (1972).

[13]R. G. Cavell, S. Kowalczyk, L. Ley, R. Pollak, B.

Mills, D. A. Shirley, and W. Perry, Phys. Rev. B 7, 5313 (1973).

[14]L. Ley, R. A. Pollak, S. Kowalczyk, and D. A. Shirley, Phys. Letters 41, 429 (1972).

[15]D. A. Shirley, Phys. Rev. B 5, 4709 (1972).

[16]J. L. Yarnell, J. L. Warren, R. G. Wenzel, and S. H. Koenig, IBM J. Res. Develop. 8, 234 (1964).

Lifetimes of Free and Bound Excitons in High-Purity GaAs

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An analysis has been carried out for obtaining the free- and bound-exciton lifetimes from optical phase shifts measured on crystals with surface loss. It is found that the bound-exciton lifetime can be obtained directly from the measured phase shifts associated with the free- and bound-exciton lines, regardless of the surface condition. The optical phase shift of the free-exciton line from a "surface-free" crystal should be larger than that measured on the same crystal but with a lossy surface. Experiments to measure the phase shifts of free excitons and excitons bound to neutral and ionized donors (D^0 and D^+) and neutral acceptors (A^0) have been carried out and the various lifetimes have been determined from the above analysis. It was found that $\tau_{D0} = 1.07 \pm 0.1$ nsec, $\tau_{D+} = 0.8 \pm 0.08$ nsec, and $\tau_{A0} = 1.6 \pm 0.6$ nsec at 1.6 °K. The free-exciton lifetime decreases with increasing impurity concentration in the material (the longest lifetime obtained being 2.9 ± 1.3 nsec), indicating that the decay of free excitons is not governed by the direct annihilation of the electron-hole pairs.

I. INTRODUCTION

The edge emission around 1.5 eV in high-purity GaAs at low temperature (< 4.2 °K) consists of several sharp lines at 1.5157, 1.5141, 1.5133, and 1.5121 eV due to recombination of both free excitons and excitons bound to donors and neutral acceptors.[1-5] The stress dependence of the line position shows that the 1.5157-eV line is due to the decay of $n = 1$ free excitons.[6,7] The line at 1.5141 eV has been identified as arising from the decay of excitons bound to neutral donors from the splitting behavior of the donor excited states in a magnetic field[4] and from the agreement[5] between the observed peak position and that expected from the electron-hole mass ratio recently calculated by Baldereschi and Lipari.[8] The decay of excitons bound to neutral acceptors has been shown from Zeeman experiments and from the temperature dependence of the line intensity[9] to be responsible for the emission at 1.5121 eV.[5] Although there has been no definite assignment of the origin of the 1.5133-eV line, it has been associated with the recombination of excitons bound to ionized donors simply because the line position is consistent with that expected from effective-mass considerations.[2,10] In this paper, measurements of lifetimes of these excitons are

reported.

Information on the lifetimes is very useful in understanding the decay mechanism of the excitons. For example, dependence of free-exciton lifetime on impurity concentration indicates that free excitons decay through impurity trapping. Comparison of the measured lifetime with the theoretical lifetime will show the importance of nonradiative processes.[11] No measurements have been reported for the lifetimes of the above excitons in GaAs. This is perhaps not surprising, since these exciton lifetimes are extremely short (~ 1 nsec), which makes real-time decay experiments impractical (instrument limited). Furthermore, the requirement of high spectral resolution because of the location of several sharp lines in a small spectral region (~ 35 meV) means that one is working with a very weak detected signal in the usual optical-phase-shift techniques.[12,13] With an improved optical-phase-shift system reported earlier,[14] we are able to measure the phase shifts associated with the various exciton lines.

It has been demonstrated that the same crystal with and without surface recombination shows different measured phase shifts associated with the free-electron–hole recombination.[15,16] In the absence of any "surface-free"[17] crystals, it is nec-