postulated degeneracy of TiS$_2$ is thought to arise from excess Ti atoms between the layers. Such an excess is found in crystals deliberately prepared metal rich or in material quenched from high temperature. In such materials basal cleavage is difficult and the crystals are brittle. The ease with which our materials can be cleaved and intercalated argues against interlayer Ti.

The implications of the present study extend to the interesting work of Barz *et al.*[10] on the layered compound Li$_x$Ti$_{1.1}$S$_2$. A recent theoretical speculation by Phillips[11] on the superconductivity in these compounds includes the assumption that TiS$_2$ has a 1-eV band gap. Before meaningful theoretical considerations of these and other intercalation compounds can be made, a more careful study of the simple dichalcogenides will be required.

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Evidence for the Polarization of Polyethylene from Positron Lifetimes*

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Four lifetimes have been resolved for positrons annihilating in polyethylene. The three longer lifetimes are identified with three kinds of morphologies in which the positrons annihilate. These lifetimes are observed to decrease with increase of applied static electric field across the polyethylene. This evidence and evidence from the intensities associated with these three lifetimes support the conclusion that polyethylene is polarized under the influence of a static electric field.

We have used positrons as a probe to elucidate the structure of polymeric solids and in particular to show that polyethylene, normally considered nonpolar, is polarized under a static electric field. Polarization, in this context, refers to electric-field-induced molecular alignment as well as field-induced charge separation. The results from initial experiments are reported here.

The annihilation time spectra for positrons annihilating in polymeric solids are complex and can be decomposed into exponentially decaying components. We have clearly resolved four lifetime components (Table I) by analytically representing the annihilation lifetime spectra for positrons annihilating in polyethylene by a sum of exponential functions convoluted with a prompt instrumental resolution function as described by Lichtenberger, Stevens, and Newton.[1] In agreement with other authors[2,3] we had only previously been able to resolve three lifetime components.[4] In an attempt to better characterize the annihilation mechanisms associated with each of these components we measured the lifetimes and intensities of positrons annihilating in polyethylene under the influence of a static electric field.

The polyethylene sample used has a weight average molecular weight of 41 700 and its ratio

TABLE I. Experimental values of the average lifetimes and intensities of positrons annihilating in polyethylene under the influence of a static electric field E.

E (kV/cm)	I_1 (%)	I_2 (%)	I_3 (%)	I_4 (%)	τ_1 (nsec)	τ_2 (nsec)	τ_3 (nsec)	τ_4 (nsec)
0	23.5	46.6	10.6	19.3	0.145	0.352	0.663	2.39
30	19.1	49.8	11.6	19.5	0.147	0.349	0.660	2.39
60	18.3	50.8	11.4	19.5	0.145	0.348	0.651	2.39
90	17.4	52.4	11.7	18.5	0.144	0.345	0.640	2.38
100	16.4	51.6	13.4	18.6	0.145	0.343	0.629	2.37
110	14.3	52.2	14.6	18.8	0.144	0.335	0.600	2.34
120	13.9	51.1	16.6	18.5	0.144	0.327	0.583	2.34

of weight average molecular weight to number average molecular weight is 3.7. The polyethylene powder was obtained from the Pressure Chemical Company[5] and was carefully molded into two uniform homogeneous disks by compressing the powder in a stainless steel mold at 170°C and allowing the mold to cool to room temperature. Each disk was 1.68 mm thick and had a density of 0.941 ± 0.005 gm cm^{-3}.

A 5-μCi ^{22}Na positron source was deposited directly on a 1.27×10^{-3}-mm-thick nickel foil disk whose diameter was considerably less than the diameter of the polyethylene disks. The nickel foil disk was sandwiched between the polyethylene disks which in turn were sandwiched between polished ground brass foil disks. The nickel foil was connected to the high-voltage terminal of a regulated, ripple-free power supply. The whole assembly was evacuated to less than 10^{-6} Torr.

A typical fast-slow coincidence system[6] with a resolving time of 280 psec (full width at half-maximum for ^{60}Co) was used to measure the positron lifetimes for static electric fields ranging from 0 to 120 kV/cm at room temperature. The two detectors were 90° with respect to each other. At each value of the electric field, positron lifetimes were accumulated over 24 h. The measurements were done in the sequence indicated in the left-hand column of Table I which contains the positron lifetimes and intensities as analyzed. Errors of ±1.5% are assigned to the lifetimes. We believe that the intensities quoted as a percentage are within 1% of the actual relative intensity.[1] Figure 1 is an example of a typical lifetime spectrum with the prompt resolution curve superimposed.

The average lifetimes τ_2, τ_3, and τ_4 decrease with increasing electric field; τ_2 decreases by 7%, τ_3 by 12%, and τ_4 by only 2%. This evidence indicates that increasing the electric field in the polyethylene produces a change in the electron density configurations in the polyethylene molecules in such a way that the amount of overlap of the positron and orbital electron wave functions increases, thus decreasing these lifetimes. We support previous suggestions[2,3,4] that the lifetime which we have labeled τ_4 is due to the pick-off annihilation of ortho-positronium (o-Ps) in the amorphous regions of the polymer that occur between spherulites. We propose, as is further discussed below, that the lifetimes τ_2 and τ_3 are due to free positrons annihilating in a singlet configuration with respect to orbital electrons in the folded-chain crystalline regions and in the less ordered regions between the folded chains within the spherulites, respectively. Thus three

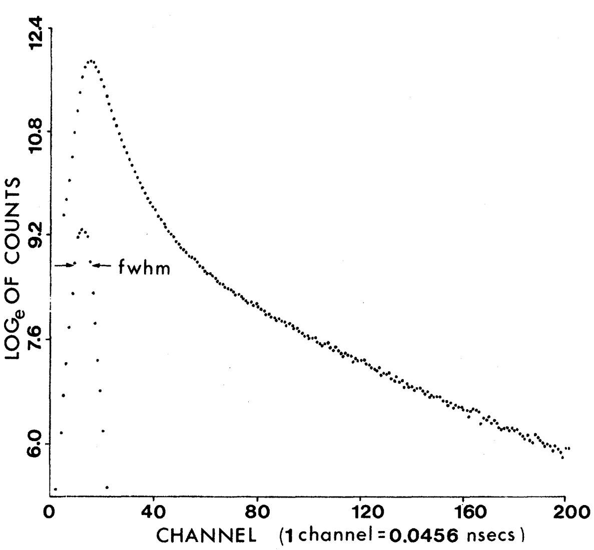

FIG. 1. Typical lifetime spectrum for positrons annihilating in polyethylene. The prompt instrumental resolution curve (full width at half-maximum, 280 psec) is superimposed and centered at time $t = 0$. Four lifetime components have been resolved from this spectrum after unfolding the prompt instrumental resolution curve (Ref. 1) (Table I, 0 kV/cm).

TABLE II. Relative intensities of positrons annihilating in the three kinds of morphologies identified in the text. Data obtained from Table I.

E (kV/cm)	$I=I_2+I_3+I_4$ (%)	$I_2'=I_2/I$ (%)	$I_3'=I_3/I$ (%)	$I_4'=I_4/I$ (%)	$I_1-I_4/3$ (%)
0	76.5	60.9	13.9	25.2	17.1
30	80.9	61.6	14.3	24.1	12.6
60	81.7	62.1	14.0	23.9	11.8
90	82.6	63.4	14.2	22.4	11.2
100	83.6	61.7	16.0	22.2	10.2
110	85.6	61.0	17.1	21.9	8.0
120	86.2	59.2	19.3	21.5	7.7

morphologies are distinguished by positrons annihilating with lifetimes τ_2, τ_3, and τ_4. We suggest that τ_1 is partly due to para-positronium (p-Ps) self-annihilation, of which statistically there must be one third as much as o-Ps. The rest of τ_1 is probably due to some short-lived bound state, possibly positron-polyethylene.

Table II presents the relative intensities of positrons annihilating in the three kinds of morphologies identified above. The relative number of positrons annihilating with these three lifetimes is given as a percent in column 2 and labeled I. The percentage of I of positrons annihilating with average lifetime τ_2 in regions with folded-chain morphology is listed in column 3 as I_2'. Similarly the percentages of I of positrons annihilating with average lifetimes τ_3 (regions of loops and cilia between the regions of folded chains) and τ_4 (amorphous regions between spherulites) are listed in columns 4 and 5 as I_3' and I_4', respectively. The percent crystallinity for the polyethylene sample used was determined for us by the Polymer Corporation, Sarnia, Ontario. Differential scanning calorimetry gives a result of 75.6%, and x-ray diffraction gives a result of 72.9%. These values of percent crystallinity are in excellent agreement with 74.8%, the sum of I_2' and I_3'.

I increases with increasing electric field as does I_3'. I_2' increases initially and then decreases. I_4' decreases, in agreement with Brandt and Feibus.[7] An increase of the electric field increases the long-range order in the polyethylene. We suggest that the rapid increase in I_3' as I_2' levels off and decreases is due to a transfer of polymer segments from a folded-chain morphology to an extended-chain morphology which has been shown to be the more stable under stress.[8] From the large ($\simeq 12\%$) decrease in τ_3 it seems to be easier to align the cilia and loops between the folded-chain regions than the entangled molecules in the amorphous region. This would be expected.

In order to check on the permanence of the polarization effects induced, we waited two days after the polyethylene had been subjected to a field of 140 kV/cm and then repeated the run at zero applied electric field. (The results of the 140-kV/cm run were not considered reliable, although the trends in the tables are preserved, since breakdown along the polymer surface occurred before sufficient statistics could be accumulated.) We found these results difficult to fit with our model. The results for I_2', I_3', and I_4' were 53%, 22%, and 25%, respectively. τ_2, τ_3, and τ_4 were 0.34, 0.58, and 2.4 nsec, respectively. Obviously τ_4 and I_4' (amorphous region) have the same values as in our initial run at zero applied electric field. The folded-chain morphology has recovered somewhat as seen from the τ_2 lifetime but I_2' remains at about the value we would have expected for the 140-kV/cm run. τ_3 and I_3' appear to be the most stable after the electric field has been removed and suggest to us an extended-chain morphology. We also repeated the 60-kV/cm run after the 140-kV/cm run and found a more difficult analysis but the trends in the tables preserved.

The percentage of positrons not trapped in any of the three morphologies or annihilating in some short-lived bound state is listed in column 6 of Table II and is seen to decrease with increasing electric field by the same amount ($\simeq 10\%$) as I increases. If τ_1 were partly due to a short-lived self-annihilating bound state, the angular correlation results of MacKenzie and McKee[9] could be explained. They observed an increase in low-momentum components in Teflon as crystallinity decreased.

The results of the temperature dependence of the lifetimes and intensities of positrons annihilating in polysyrene (to be reported[10]) will be summarized in support of the above discussion. We find three components in this glass. I_1 ($\simeq 35\%$) is due to free positrons not trapped or in some short-lived bound state ($\simeq 20\%$) and p-Ps ($\simeq 15\%$). I_2 ($\simeq 27\%$) is due to the annihilation of free positrons in regions of order due to nodules[11] or spherically symmetric strain fields.[12] I_3 ($\simeq 38\%$) is due to the annihilation of positrons in the amorphous regions by pickoff of o-Ps. A plot of τ_3 ($\simeq 2$ nsec) versus the temperature T shows a linear relationship with positive slope, changing to a steeper positive slope at the glass transition.[6] A plot of τ_2 ($\simeq 0.4$ nsec) versus T shows a linear relation with positive slope, similar to τ_3 versus T, below the glass transition where τ_2 changes abruptly from about 0.42 to 0.47 nsec. Thus the glass transition seems to consist of a combination of first-order and second-order transitions. The lifetime of the τ_1 component changes abruptly from 0.13 nsec in the glass to about 0.16 nsec in the highly viscous liquid. While results for temperatures below the glass transition were easily fitted by our model, results for temperatures above the glass transition (highly viscous liquid) were difficult to fit, although the data fit three components better than two or four. Experiments to measure the temperature dependence of positron lifetimes and intensities in polyethylene and to continue the electric field experiments for polar molecules, such as Teflon, are planned.

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Close Similarity between Photoelectric Yield and Photoabsorption Spectra in the Soft-X-Ray Range

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Because of the similarity between photoelectric yield and photoabsorption spectra in the soft x-ray region, "yield spectroscopy" can be used as a successful method for investigating fine structure in the electronic excitation spectra of solids. The continuous spectrum of synchrotron radiation is especially appropriate for such measurements. We reinvestigated the structure of the $4d$ excitations in Pr and the $2p$ excitations of Si using a single crystal.

Using the continuous spectrum from a soft-x-ray tube, Lukirskii and co-workers[1,2] established a close similarity between photoelectric yield and absorption spectra for core excitations in several materials, mainly alkali halides. There are, however, only a few yield measurements available which allow a comparison in the low-energy region. Good agreement is found for the $L_{2,3}$ spectrum[3] of Na in NaCl around 30 eV. At even lower energies the $3p$ excitations of K in the potassium halides[4,5] around 20 eV can be identified in both absorption (ϵ_2) and yield spectra; the actual shape, however, of the structure is quite distorted in the yield spectra. The valence-band