Photoemission band symmetries and dipole active modes of crystalline films of vinylidene fluoride (70%) with trifluoroethylene (30%) across the ferroelectric transition(s)

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Abstract. The symmetry of the occupied electronic bands of crystalline films of vinylidene fluoride (70%) with trifluoroethylene (30%) and the vibrational dipole modes are identified using angle resolved photoemission and high resolution electron energy loss respectively. The symmetry of the occupied valence bands is preserved across the surface 'ferroelectric' phase transition. The temperature dependent changes in the electronic structure occur primarily in the conduction band and are accompanied by a surface dipole reorientation and a surface Brillouin zone doubling across the surface transition, thus these results strongly support a first order transition with a uniaxial polarization direction in these crystalline ferroelectric polymer films. There is compelling evidence that this surface phase transition is an improper ferroelectric transition and discontinuous.

Ferroelectric phase transitions have often been discussed in terms of the Landau model of phase transitions [1–6]. As such, the symmetry can have a profound influence on our understanding of the ferroelectric transition [7]. The lattice polarization can cause shifts in the critical points of the band structure in both the ferroelectric perovskites [8] and the ferroelectric polymers [9, 10]. In the case of the ferroelectric polymers, the unoccupied band structure has been observed to change significantly across a surface 'ferroelectric' transition [9, 10]. The accompanying changes in symmetry and selection rules have a significant impact on whether we treat polarization as a possible order parameter (or not), in the context of mean field theory [6, 7, 11, 12].

The surface 'ferroelectric' phase transition has been identified at $20\,^\circ\text{C}$ in ferroelectric vinylidene–fluoride polymers, distinct form the first order [13] bulk ferroelectric transition at $80\,^\circ\text{C}$ [10, 14, 15]. The surface transition exhibits maxima in the dielectric constant, the pyroelectric response, the conductivity, and a sharp increase in the density of states near the Fermi level, all with thermal hysteresis [14, 15]. This suggests, but is not compelling proof of a first order phase transition.

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In this paper, we probe the symmetry of the occupied bands of crystalline films of vinylidene fluoride (70%) with trifluoroethylene (30%), across both the bulk and surface coupled ferroelectric–structural phase transitions, using angle resolved photoemission.

The films were formed by Langmuir–Blodgett monolayer deposition from water subphase as described elsewhere [16, 17]. The films were deposited on silicon for the angle resolved photoemission studies. The synchrotron radiation, at the Center for Advanced Microstructure and Devices (CAMD) synchrotron light facility, was dispersed by a plane mirror grating monochromator beamline described in detail elsewhere [18]. The films were prepared by gentle annealing to 150 °C *in vacuo* and surface composition characterized with core level spectroscopy (XPS) and inverse photoemission (IPES) as described previously [9, 10, 14]. The electron energy loss spectroscopy (EELS) was undertaken using an LK-2000 spectrometer at Oak Ridge National Laboratory. Thinner samples were essential for the electron spectroscopies to avoid excessive charging of the sample surface. The temperature was determined using a chromel–alumel thermocouple.

The vibrational modes determined from high resolution electron energy loss are compared with a semi-empirical calculation for a molecule of four monomers of vinylidene fluoride and two monomers of trifluoroethylene for both the all-*trans* configuration and the alternative *gauche* and *trans* configuration structures. The vibrational modes were calculated with a MNDO-PM3 (modified neglect of differential overlap, parametric method 3) Hamiltonian. This Hamiltonian does not include solid state effects and dipole–dipole coupling. The geometrical structures are optimized (C_{2v} for the all-*trans* configuration and C_s for the alternative *gauche* and *trans* configuration) and the vibrational modes then calculated. The results of this semi-empirical calculation were compared with the *ab initio* calculation obtained from the Gaussian method with the STO-3G basis set, in a fashion similar to that undertaken for adsorbed molecules elsewhere [19]. The latter *ab initio* calculations show a larger deviation from experiment, so we restrict the discussion here to a comparison with the semi-empirical calculations.

The polarized light incidence angle was used to vary the selection rules in angle resolved photoemission by changing from more s-polarized light (near normal light incidence) to more p-polarized light (near grazing light incidence angle, or incidence angles away from the surface normal). As seen in figure 1, there are dramatic changes in the photoemission spectra of 5 monolayer crystalline films of vinylidene fluoride (70%) with trifluoroethylene (30%) with changing light incidence angle. The orientation of the polymer chains is established [9, 10] and the films of vinylidene fluoride (70%) with trifluoroethylene (30%) are well ordered and crystalline [9,10], as shown by low energy electron diffraction (LEED) [9, 10], scanning tunnelling microscopy (STM), band structure mappings [9, 10] and x-ray diffraction (XRD) [10]. Thus, this light incidence angular dependence in photoemission can be used to assign the symmetry of the occupied (valence) bands [20–23].

The principle of symmetry selection lies within Fermi's golden rule, as is typically applied to photoemission [20–23]:

$$d\sigma/d\Omega \sim |\langle\varphi_f|H'|\varphi_i\rangle|^2\{\delta(E_f - E_i - h\nu)\} \qquad (1)$$

where H' is the perturbing Hamiltonian and is proportional to $\boldsymbol{A} \cdot \boldsymbol{p} + \boldsymbol{p} \cdot \boldsymbol{A}$ (or to the dipole operator $\boldsymbol{e} \cdot \boldsymbol{r}$) where $\boldsymbol{A}$ is the vector potential of the incident and polarized light, φ_i is the initial state and φ_f is the final state, of which the latter is the fully symmetric wavefunction. The perturbation to the Hamiltonian, $H' = \frac{1}{2}(\boldsymbol{A} \cdot \boldsymbol{p} + \boldsymbol{p} \cdot \boldsymbol{A})$ is usually further simplified (at least for smaller molecules) by assuming that $\boldsymbol{p} \cdot \boldsymbol{A} \propto \nabla \cdot \boldsymbol{A} \approx 0$ (the spatial variation of the light field is small on the atomic or molecular scale). The cross section depends on the initial state, final state (whose parity is always even), light polarization and dipole moment

field of the sample. Based on this polarization dependence, the symmetry of the initial state wavefunction can be investigated.

The symmetry of the surface Brillouin zone is now established to be C_{2v} ($mm2$) by STM, LEED and the unoccupied band structure [9], while the symmetry of the real space surface structure is thought to be $C_{1h}(m)$ or $C_{2h}(2/m)$ for crystalline films of vinylidene fluoride (70%) with trifluoroethylene (30%) [9, 10] as summarized in figure 2. The chains are aligned in the plane. Assuming the highest possible symmetry available from surface structural studies (C_{2v}), we can use selection rules to assign the symmetry of the photoemission features. In figure 1, we collected the photoelectrons normal to the surface to preserve the high possible point group symmetry. Molecular orbitals of a_1 (s, p_z, $d_{3z^2-r^2}$) symmetry (where z is along the surface normal) have no amplitude along the molecular axis (say along x), for normal emission. This means that if the polarization of the incident light is arranged so as to have the vector potential $\boldsymbol{A}$ along the molecular axis (small incidence angle with respect to the surface normal), $\boldsymbol{A} \cdot \boldsymbol{p}$ has b_1 (p_x, d_{xz}) or b_2 (p_y, d_{yz}) symmetry. For photoemission to be allowed with this polarization and detection geometry, the initial state must also be of b_1 or b_2 symmetry to couple to the allowed final state. With the vector potential perpendicular to the molecular axis (along z or the surface normal), i.e. large light incidence angles with respect to the surface normal), $\boldsymbol{A} \cdot \boldsymbol{p}$ has a_1 symmetry, and only a_1 symmetry initial states are allowed with the electron energy analyser detecting only those photoelectrons with wavefunction symmetric to all symmetry operations of surface plane.

In figure 1(a), we show the light polarization dependence of the photoemission spectra at 173 K, well below both the surface and bulk ferroelectric transitions. Based on the light incidence angle dependence, we assign the symmetry of the various bands as indicated in figure 1. These bands appear at the binding energies of 8.2 eV (b_1, b_2), 10.9 eV (b_1, b_2), 11.8 eV (a_1), 14.95 eV (b_1, b_2) and 16.3 eV (a_1).

At higher temperatures, as seen in figure 3, the binding energies of the photoemission features shift towards smaller binding energies, while the unoccupied levels, as derived from inverse photoemission [9], also shifts toward the Fermi level. The symmetry does not change, however, as indicated by the very similar light polarization dependence in figure 1. The substantial part of the shift in binding energies, in photoemission, does *not* correspond to the surface or bulk ferroelectric phase transitions as the shifts occur well below 250 K, as summarized in figure 3. There is a low temperature phase transition, recently identified, that is correlated with the shift in binding energy and is discussed in detail elsewhere [24]. The preservation of band symmetry across the ferroelectric transition(s) is quite unlike the ferroelectric perovskite oxides where symmetry changes are both expected [8] and observed and is quite unexpected.

The surface transition at 290 K to 300 K (20 °C) [9, 10, 14] is clearly associated with a dipole reorientation or dipole misalignment. The spectra in figure 4 are deconvoluted into six vibrational bands, as suggested by the semi-empirical calculations described below. The vibrational mode at around 450 cm^{-1} is mostly related to the CF_2 bending mode and this is dipole active below the surface 'ferroelectric' transition in high resolution electron energy loss (HREELS) (at 110 K and 270 K, as seen in figure 4). The assignment and energy is in good agreement with the experimental [25] and theoretical [26] values for PVDF at 442 and 430 cm^{-1} respectively. The two dipole active modes at approximately at 900 cm^{-1} (the CF_2 and CH_2 rocking modes) and 1150 cm^{-1} (the CF_2 stretch mode and CH_2 rocking mode) can be identified in high resolution electron energy loss (HREELS) at 110 K and 270 K as well (figure 4). For other studies of PVDF, the CF_2 and CH_2 rocking modes have been experimentally identified at 880 cm^{-1} [25] and theoretically at 897 cm^{-1} [26], while the combined CF_2 stretch mode and CH_2 rocking mode is at 1177 cm^{-1} in experiment [25] and 1180 cm^{-1} in theory [26]. These
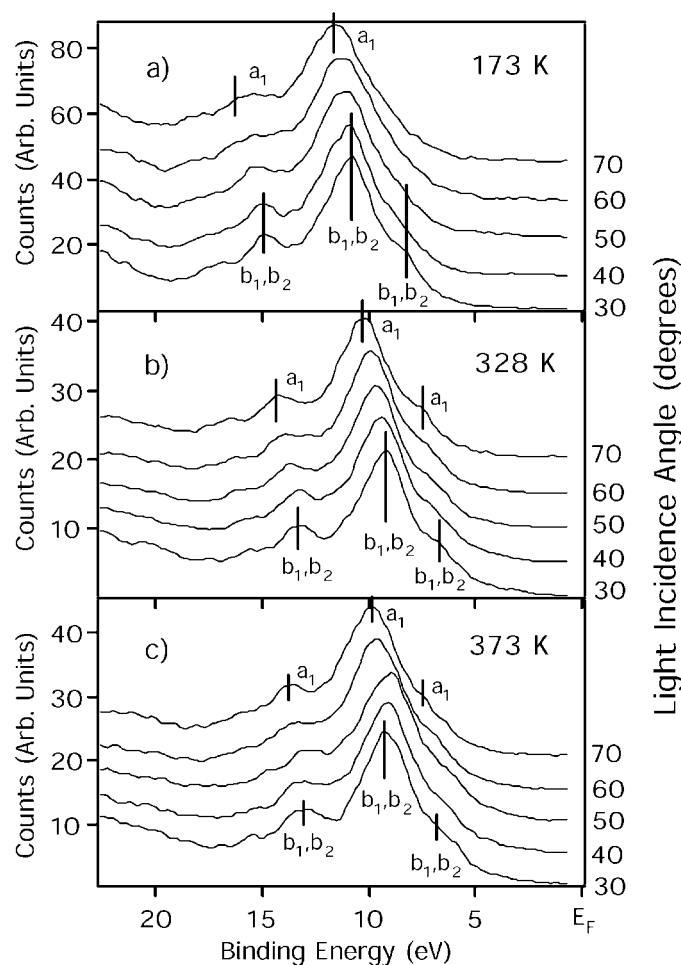
Figure 1. The valence band photoemission spectra as a function of light incidence angle (with respect to the surface normal at (a) 173 K, (b) 328 K and (c) 373 K. The photoelectrons were collected normal to the surface and the photon energy is 42 eV. The polarization of the light is varied as a function of light incidence angle, with respect to the surface normal, in the mirror plane. Large angles represent more p-polarized light and small angles constituting more s-polarized light.

dipole modes are characterized by relatively stronger intensities in the specular scattering geometry as compared to the off-specular scattering geometries. The modes at 1300 cm^{-1} (CH_2 wagging and CC stretch mode), 1600 cm^{-1} (CH_2 bending mode) and 2900 cm^{-1} (CH_2 stretch mode) are stronger in off-specular scattering than in on-specular and are therefore certainly not dipole active modes.

As the temperature increases to 315 K and above, the dipole character of the 450, 900 and 1150 cm^{-1} modes is lost with the scattering plane parallel with the P(VDF–TrFE) chains (as seen in figure 4), but not with the electron energy loss scattering plane perpendicular to the chains. The loss of dipole character in the 450 and 1100 cm^{-1} modes could be because, overall, the surface dipole are reoriented away from the surface normal, or because the root mean square displacement of the surface dipoles away from the surface normal is very large. The results favour the latter explanation rather than a reorientation of bond directions away from
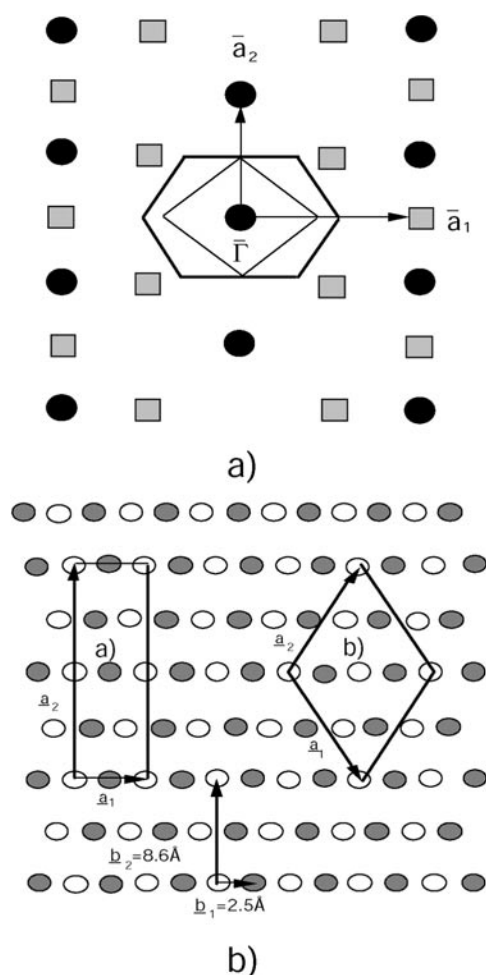
Figure 2. (a) The postulated surface Brillouin zones below the surface 'ferroelectric' transition (thick lines–circles for reciprocal lattice points) and above the surface 'ferroelectric' transition (thin lines and both circles and squares for the reciprocal lattice points). (b) Both postulated real space lattice(s) of the surface [8, 9].

the surface normal. The absence of change in the occupied electric band symmetries and the absence of change in the dipole character of the 450, 900 and 1100 cm^{-1} modes in the scattering geometry perpendicular to the P(VDF–TrFE) chains strongly suggests that there is an increase in the average displacement of the dipoles away from the surface normal with increasing temperature across the surface 'ferroelectric' transition. The increased dynamic motion of the dipoles at temperatures greater than the surface 'ferroelectric' transition is consistent with the fluctuations in surface structure at higher temperature [10] and the change in work function [9] and the expected tendency of the dipoles to exhibit dynamic 'wagging' motion perpendicular to the chains.

The loss in intensity of the strong dipole modes at the high temperatures, in particular the dipole mode at 450 and 900 cm^{-1} can only partly be explained by a dipole reorientation as indicated in figure 5. A comparison of the expected vibrational intensities for the all-*trans* configuration of the polymer (the ferroelectric phase) is somewhat more intense than the
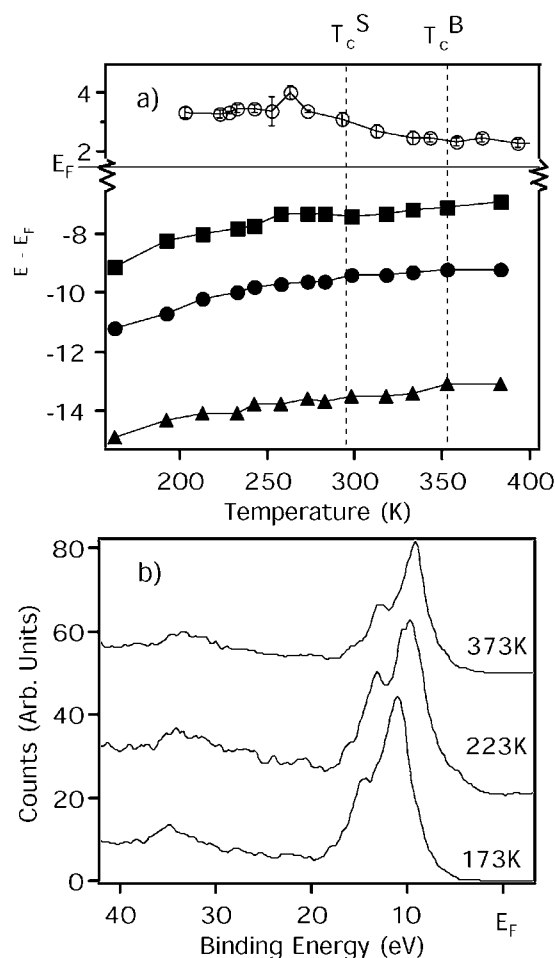
Figure 3. (a) The binding energy shift of the lowest unoccupied molecular orbital and several of the occupied molecular orbitals as a function of temperature. The temperature dependence of the unoccupied level is taken from inverse photoemission [9, 10] while the binding energies of the occupied levels are derived from photoemission. (b) The temperature dependence of the valence band photoemission spectra, for normal emission and a mixture of s and p polarized light (45 degrees light incidence angle) using a photon energy of 74 eV.

vibrational intensities for the alternating *trans–gauche* configuration for P(VDF–TrFE) or the 'classic' paraelectric phase configuration [10]. We also expect an influence from screening of this dipole mode and increase in the Drude tail of the elastic peak as the surface becomes more metallic in character with increasing temperature [14].

The absence of changes in band symmetries, with increasing temperature across the surface 'ferroelectric' phase ($T \approx 20\,°\mathrm{C}$) and bulk phase ($T \approx 80\,°\mathrm{C}$) transitions, has profound consequences. In the context of the Landau theory of phase transitions, the free energy is written in terms of the order parameter $p_s(r)$ as:

$$F = \int [Dp_s(r) + Ap_s^2(r) + Bp_s^3(r) + Cp_s^4(r)]\,\mathrm{d}x\,\mathrm{d}y \qquad (2)$$

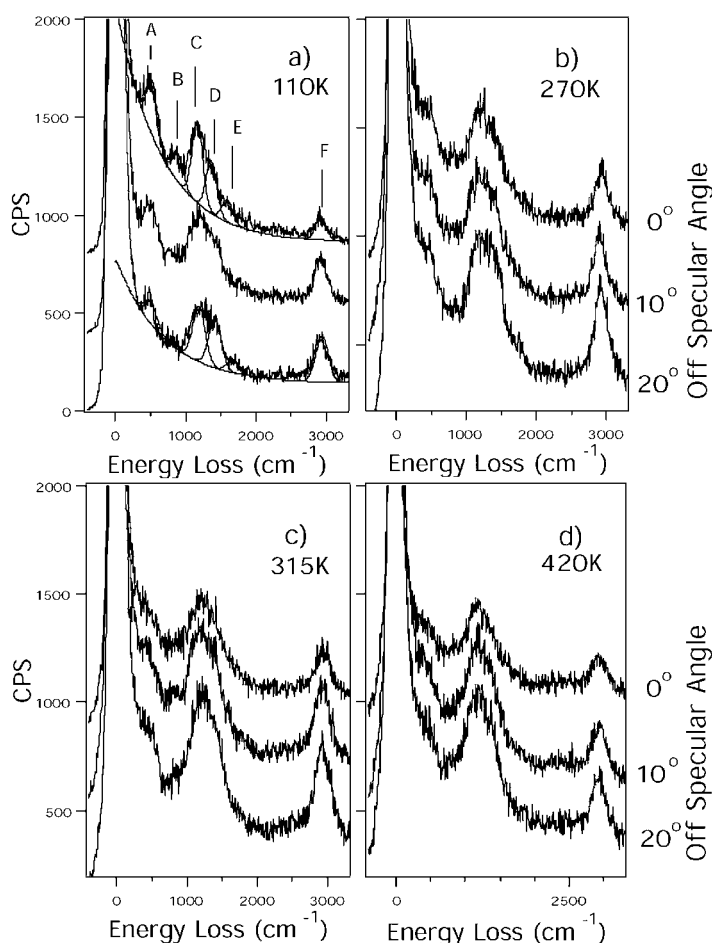neglecting, as is typically done, the higher order terms. (Because the surface normal is along

Figure 4. Comparison of the specular and off-specular electron energy loss spectra are taken along the polymer chain of 2 monolayer copolymer P(VDF–TrFE) films at 110 K, 270 K, 315 K and 420 K. We identify the observed vibrational modes as peaks A: mostly related to the CF_2 bending mode and dipole active; B: the CF_2 and CH_2 rocking modes; C: the combined CF_2 stretch mode and CH_2 rocking mode; D: the CH_2 wagging and CC stretch mode; E: the CH_2 bending mode; and F: the CH_2 stretch mode. The kinetic energy of the incident electron is 3.71 eV and the incidence and emission angle of the electron is 60° with respect to the surface normal. The pass energy is 2.70 eV.

$\langle z \rangle$, we integrate in the x–y plane.) A–D are coefficients that depend upon variables like temperature and pressure. With a symmetry change between the structure of the ferroelectric thin film and the nonferroelectric or paraelectric film, the coefficient $D = 0$ [7, 27, 28]. For $D \neq 0$ there is no phase transition in Landau theory; the linear term must be zero by symmetry constraints. The order parameter, $p_s(r)$, may well be something other than polarization and cannot be explicitly defined as yet for these transitions.

The cubic term results in the abrupt change of the thermodynamic function thus if either of the odd powers exist, i.e. D or B is nonzero, then the transition is a first order transition [7, 27–29] and the phase transition is discontinuous. A second order phase transition requires the absence of the cubic term and a transition from one group symmetry to a *subgroup* symmetry (i.e. a lower symmetry subgroup of the same original group). When these conditions are
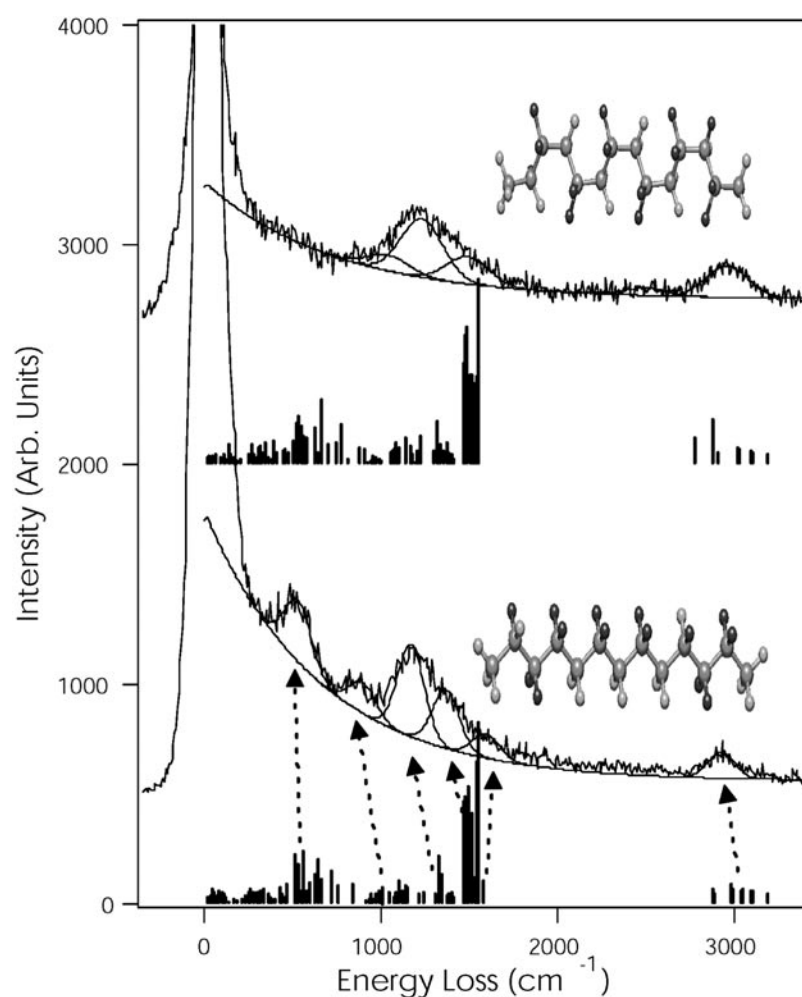
Figure 5. A comparison of the calculated vibration modes for the all-*trans* configuration and the alternating *trans–gauche* configuration of P(VDF–TrFE) with the experimental electron energy loss spectra taken at 420 K for the spectrum at top and 110 K for the spectrum at the bottom. Shifts from solid state effects and dipole–dipole coupling, not included in the calculations, can be anticipated.

satisfied, a renormalization group analysis must establish that there is a stable fixed point for the transition to be second order. A first order phase transition has no stable fixed point [7, 29]. For this film, a vertical displacement (along the surface) in structure or polarization may require a cubic term in the Landau formalism and thus would be first order.

We can see from photoemission that there is no change in the band symmetries, and the surface Brillouin zone symmetry does not change [9, 10] across either the bulk or surface 'ferroelectric' transitions. On the other hand, the dipole character of the strong dipole active modes at low temperature is lost with increasing temperature. This argues in favour of a first order phase transition across the surface phase transition at 20 °C with uniaxial polarization or a displacement in the context of Landau theory. In the case of the surface phase transition at 20 °C, there is a period doubling along the chains as indicated by the structural data [9, 10]. So

while the reciprocal lattice symmetry is preserved (C_{2v} to C_{2v}), the electron–phonon coupling is driven by phonons at $q \approx \pi/a$ not $2\pi/a$ so the phonons do not lock with the lattice electronic structure at a reciprocal lattice vector [9]. The super-periodicity, with changes in the dipole along only the surface normal requires a least one cubic (third order) term in addition to the fourth order terms. This precludes a stable fixed point.

The above arguments from Landau theory indicate that the cubic term in the free energy, forcing the transition to be a first order phase transition, is necessary across the surface (20 °C) 'ferroelectric' transition and further the cubic term is consistent with the observed uniaxial polarization direction normal to the film [30]. In real space, the only possible representation changes occur from C_{1h} ($m/2$) or C_{2v} ($mm2$) to C_{2v} symmetry or lower (C_2 or C_{1h}). The breaking of inversion symmetry that allows us to invoke a cubic term in the free energy equation (equation (2)) is certainly a consequence of the surface macroscopically breaking symmetry (i.e. the surface is not D_{2h}). This does not rule out the possibility that there is a breaking of inversion symmetry along the surface normal that is intrinsic. Whether the existence of the cubic term is intrinsic or not, the period doubling dictates that the surface phase transition is not a proper ferroelectric phase transition: the polarization cannot be the sole or necessarily even the principal order parameter.

The bulk ferroelectric transition in P(VDF–TrFE) is associated with a rotation of the polar groups around the molecular chain axis and is connected with the disappearance of all-*trans* chains to various combinations of *cis* (*gauche*) and *trans* bonds packed with little or no net dipole moment [30] but the symmetries must be preserved across the ferroelectric transition(s). Structural changes at the surface will have a significant signature in the surface dipole and bond orientation but also, from the data reported here preserved symmetry. A reorientation of the fluorine from below the plane in the ferroelectric phase to all other orientations is not possible. Locally, the surface structural transition must be abrupt, though on a large scale (a large volume of polymer) the structure can fluctuate.

Complications do exist, and we note that there is a region near criticality where the Landau theory is not valid because of fluctuations in the order parameter p_s becomes large. At 25 °C, these is no distinct symmetry dependence of the bands observed in photoemission. This is consistent with large fluctuations at the surface 'ferroelectric' transition in the Landau model (page 444, 471 in [7]).

Another complication is that in photoemission the surface breaks the symmetry, as we have noted. Thus we are hindered from ascertaining if the bulk transition is accompanied by a symmetry change along the surface normal. For example, a symmetry change from C_{2v} ($mm2$ in the ferroelectric phase) to D_{2h} (mmm in the paraelectric phase) or a change from C_{1h} ($m/2$) or C_2 (m) symmetry to C_{2v} or D_{2h} (mmm) symmetry is possible. Photoemission, therefore can tell us little about the symmetry change or does not provide similar detailed insight into the nature of the bulk transition. Nonetheless, the bulk ferroelectric phase transition at 80 °C has been experimentally shown to be first order [13, 30] and the presence of a cubic term (and hence the necessity of a first order transition) with D_{2h} has been noted by Landau and Lifshitz [7].

For a thin film, thick enough to exhibit bulk or three dimensional behaviour away from the transition, as one approaches the transition, the length scale of the fluctuations in the order parameter may exceed the film thickness and two dimensional behaviour will be established. The shift in position from chain to chain, postulated on the basis of structural studies [10], must now be a commensurate slip to preserve the band symmetry as is observed.

Consistent with the above application of the Landau model to both the structural data and the angle resolved photoemission data, as we have already noted, we observed that the surface phase transition at 20 °C exhibits thermal hysteresis [14, 15], consistent with a first order

transition. This means that the surface transition is an improper ferroelectric transition [31]. Thus the free energy equation (equation (2)) is very likely influenced by an order parameter with cross terms involving components with the stress–strain tensor or some other parameter that drives the electronic transition. The stress–strain tensor component contributions to the order parameter are certainly implicated by the imperfect doubling (not exactly by a factor of 2) of the Brillouin zone across the surface 'ferroelectric' transition [9, 10].

Further tests of this scenario for a discontinuous improper phase transition could be undertaken by looking for a discontinuity of the specific heat across the surface phase transition, or by looking for more evidence of a displacement vector along the surface normal. The implicit uniaxial polarization along the surface normal, as well as the symmetry breaking introduced by the surface, has been confirmed in large measure by independent recent optical second harmonic generation studies across the surface 'ferroelectric' transition of Langmuir–Blodgett grown films of the same P(VDF–TrFE) copolymer studied here [32].

Basically the arguments used here are similar (though not identical) to those that apply to the second and first order magnetic reorientation transitions in iron [33] where symmetry breaking of the dihedral mirror operation (symmetry breaking with the magnetic dipole aligned along the surface normal) also forces the transition to be a first order transition and discontinuous.

In summary, the temperature dependence of the valence band symmetries is consistent with an improper first order phase transition with a uniaxial polarization axis across the surface 'ferroelectric' phase transition at 20 °C [9, 10, 14] which is discontinuous. We would anticipate that there is a discontinuity of the specific heat across the surface 'ferroelectric' phase transition.

Acknowledgments

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