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Changes in Electron-Phonon Coupling Across a Bulk Phase Transition in Copolymer Films of Vinylidene Fluoride (70%) with Trifluoroethylene (30%)

C. N. Borca
University of Nebraska - Lincoln

Shireen Adenwalla
University of Nebraska-Lincoln, sadenwalla1@unl.edu

J. Choi
Louisiana State University, Baton Rouge, LA

Lee Robertson
Oak Ridge National Laboratory, Oak Ridge, TN

H. You
Argonne National Laboratory, Argonne, IL

See next page for additional authors

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Authors
C. N. Borca, Shireen Adenwalla, J. Choi, Lee Robertson, H. You, V. M. Fridkin, S. P. Palto, N. Petukhova, Stephen Ducharme, and Peter A. Dowben

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Changes in Electron-Phonon Coupling Across a Bulk Phase Transition in Copolymer Films of Vinylidene Fluoride (70%) with Trifluoroethylene (30%)

C.N. Borca,[1] S. Adenwalla,[1] J. Choi,[2] Lee Robertson,[3] H. You,[5] V. M. Fridkin,[4] S.P. Palto,[4] N. Petukhova,[4] S. Ducharme,[1] and P.A. Dowben[1]

[1]*Dept. Physics & Astronomy, and Center for Mat Res& Anlaysis, Univ. Nebraska, Lincoln, 68588*

[2]*Center for Advanced Microstructure & Devices, Louisiana State University, Baton Rouge, LA 70806*

[3]*High Flux Isotope Reactor (HFIR), Oak Ridge National Laboratory, Oak Ridge, TN 37831*

[4]*Inst. Crystallography, Russian Academy of Sciences, 59 Leninsky Prospekt, 117333 Moscow, Russia*

[5]*Materials Science Division, Argonne National Laboratory, Argonne, IL 60439*

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[1]C.N. Borca, [1]S. Adenwalla, [2]J. Choi, [3]Lee Robertson, [5]H. You, [4]V.M. Fridkin, [4]S.P. Palto, [4]N. Petukhova, [1]S. Ducharme, and [1]P.A. Dowben

[1]Department of Physics and Astronomy and the Center for Materials Research and Analysis, University of Nebraska, Lincoln, Nebraska 68588-0111

[2]Center for Advanced Microstructure and Devices, Louisiana State University, 6980 Jefferson Highway, Baton Rouge, Louisiana 70806

[3]High Flux Isotope Reactor (HFIR), Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

[4]Institute of Crystallography, The Russian Academy of Sciences, 59 Leninsky Prospekt, 117333 Moscow, Russia

[5]Material Science Division 223, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, Illinois 60439

Corresponding author:

Peter A. Dowben
Department of Physics and Astronomy
And the Center of Material Research and Analysis
Behlen Laboratory of Physics
University of Nebraska
Lincoln, Nebraska 68588-0111
Tel: 402-472-9838
Fax: 402-472-2879
e-mail: pdowben@unl.edu

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Abstract

We present evidence for a change in electron – phonon coupling across a bulk phase transition. Below the lattice stiffening transition at around 160 K, there is a change in the diffracted peak width observed by neutron and X-ray scattering techniques. Also, the electronic band structure of the copolymer is shifting in binding energy below 160 K, decreasing the density of states near the Fermi level. The value of the effective Debye temperature above the transition temperature is approximately 50 K, while below 160 K, the value of the Debye parameter is 245 K. We postulate that the coupling between electrons and phonons results in a static distortion of the lattice (below 160 K), and this distortion "melts" above 160 K.

Changes in electronic band structure induced by lattice vibrations occur mainly at the surfaces of metals or metal alloys [1,2]. Recently it was discovered that such modifications can occur throughout the entire bulk, in high-T_c copper oxides [3]. More interesting are the studies of the coupling between electrons and phonons in correlated metallic organic systems such as the Berchaard salts [4] and TTF-TCNQ (tetrathiafulvalence-tetracyanoquinodimethane) [5]. In this paper we present evidence for changes in electron-phonon coupling through a bulk phase transition discovered recently [6] in a material with almost no density of states at the Fermi level and no apparent Fermi level crossings of any sort.

The films of the P(VDF-TrFE, 70:30) copolymer were prepared using a horizontal Langmuir-Blodgett method described in detail in [7]. There are three distinct phase transitions identified in this ferroelectric copolymer. At 350 K there is a ferroelectric to paraelectric first-order phase transition with a coexistence of phases near the critical temperature [8]. The surface alone goes through a ferroelectric phase transition at 290 K associated with a conformational change of the monomers in the surface polymer chains [9]. The third phase transition occurs at a temperature of 160 K and is associated with a change in the compressibility of the crystalline lattice of the copolymer [6]. The latter transition shows no change in the dielectric response of the material in the normal direction.

The neutron diffraction measurements were taken at the HB 1A diffractometer at the High Flux Isotope reactor (HFIR) at Oak Ridge National Laboratory. The neutrons wavelength used was 2.357 Å. X-ray diffraction measurements (XRD) were performed on a Rigaku rotating anode source with Cu K_α radiation (λ=1.54 Å). For both X-rays and neutrons, the data were taken from the <010> out of plane scans, with the scattering vector perpendicular to the plane of the film. The measurements reported here were performed on a 5 monolayer (ML) sample for

XRD and 100 ML sample for neutron diffraction, though additional samples at different thicknesses were also studied. The electron energy loss spectroscopy (EELS) was undertaken using a LK-2000 spectrometer on thin samples (2 ML), in order to avoid excessive charging of the surface.

Figure 1 shows the results obtained from fitting the neutron elastic diffraction peak corresponding to a distance of 4.5 Å between chains, in the direction normal to sample surface. The peak was fitted to a Lorentzian after background subtraction. Figure 1 (a) shows the amplitude of the elastic peak, while Figure 1 (b) presents the full width at the half maximum (FWHM) of the same peak. The temperature dependence of the peak intensity was presented in [6, 10], and was fitted with the well known attenuation law $I(T)=I_0 \exp[-2W(T)]$, where $W(T)$ is the Debye-Waller factor. One can regard the empirical parameter θ_D, the Debye temperature, as a measure of the "stiffness" of the crystal. Above 200 K the data agrees with an effective Debye temperature of 48 ± 2.4 K, while below 160 K, the results are consistent with a value five times greater (250 ± 12.5 K) for the effective Debye temperature [6].

Using an unpolarized light source (and a detector with large acceptance angle, ±10°), we have calculated the effective bulk Debye temperature using the temperature dependence of the PES spectra [10] obtained for a 5 monolayer sample. Surface contribution was minimized by choosing a particular band that had mostly bulk weight (binding energy shifts when the energy of the incoming photons is changed). The value obtained from PES was 53 ± 11 K which is very close to the Debye temperature obtained from neutron diffraction above the stiffening transition temperature [6]. Analyzing the separate contributions to the neutron scattering peak intensity, we can observe that the FWHM as well as the peak amplitude in Figure 1 decrease with increasing temperature. The FWHM behavior with temperature is unexpected. This increase in the FWHM,

at low temperatures, suggests that the coherence of the chain-to-chain planes diminishes as the temperature is lowered below 160 K. A calculation of the coherence length can be done using the Debye-Scherrer formula:

$$L_C = \frac{0.9\lambda}{\Delta 2\theta \cos \theta_B}$$

where $\lambda = 2.357$ Å is the neutron wavelength, $\Delta 2\theta$ is the FWHM in 2θ radians, and θ_B is the Bragg elastic diffraction peak. For the high-temperature phase the coherence length is ~ 130 Å, whereas for the temperature region below 160 K, the coherence length drops to ~ 35 Å, for the 100 ML film. This behavior is similar to the one obtained from X-ray diffraction [8], where a similar calculation showed a three times drop of the coherence length at low temperature compared to high temperature.

There are several key pieces of evidence to support the existence of electron-phonon coupling in this system. Using X-ray diffraction for the same lattice spacing (4.5 Å) as the one studied with neutrons, we were able to determine the temperature dependence of the FWHM and amplitude of the elastic peak. As shown in Figure 2 (a) and (b), the amplitude and FWHM of the X-ray diffraction peak exhibit a strong anomaly around 160 K. The FWHM increases, while the peak amplitude decreases in a relatively short temperature range. It is well known that X-ray diffraction is sensitive to electron cloud distributions, mainly to the fluorine (and to a lesser extent, carbon) electrons in our samples. Therefore, the XRD data indicates that fluctuations in the electron cloud, normal to the film, are the cause of the anomaly in temperature around 160 K of the FWHM and amplitude of the diffracted peak.

Figure 3 presents the temperature dependence of the intensity and FWHM obtained from an EELS study [11] of the phonon modes in P(VDF-TrFE, 70:30) copolymers. Two dipole active optical modes were identified in the energy loss spectrum, characterized by stronger intensities in

the specular scattering geometry as compared to the off specular geometries. The intensity and FWHM for both phonon modes have similar temperature dependence as seen in Figure 3. The dipole is formed inside each monomer between the relatively electronegative fluorine to the hydrogen. The dipole active phonon modes probed in EELS are intra-chain modes, parallel to the surface normal. As the temperature increase, the FWHM of the phonon modes increases while the intensity of the modes decreases, resulting in a loss of harmonic vibrations between dipoles, and the presence of a surface phase transition, as shown in [11].

Studying the electronic structure of the P(VDF-TrFE, 70:30) copolymers, we have observed enhanced insulating properties in photoemission spectroscopy (PES) in the form of binding energy shifts of the valence band. As presented in [6], the binding energy increases with approximately 2.2 eV between 163 K and 210 K, consistent with the onset (at the high temperature end) of the lattice stiffening transition at about 200 K. This shift is expected of final state effects [12] associated with an increasingly smaller in-plane screening parameter [13] or a surface photovoltage effect [13,14]. This strongly indicates the existence of electron-phonon coupling above the stiffening transition temperature of 160 K.

Below the stiffening temperature, the electronic band structure is perturbed by the lattice vibrations/distortions as indicated by the shift in photoemission electron binding energy [6] of the valence band. On the other hand, from neutron diffraction, the FWHM of the elastic peak reaches the maximum value for temperatures below 160 K, as can be seen in Figure 1. This implies that the chains are frozen in a static distortion, and the coherence between planes in the normal direction diminishes. The stiffening of the lattice, in a state with less order between chains, influences the bulk Debye temperature by increasing its value five times, from 48 K to 250 K. We believe that coupling between a distorted lattice and electrons should change across

the transition temperature. Unfortunately, we have not enough resolution in our PES results to calculate the value of the electron-phonon mass enhancement parameter λ_s, as in [15]. We expect the parameter λ_s to increase below the stiffening transition at 160 K, indicating a strong electron-phonon coupling in the low temperature regime. Above 160 K, the electron-phonon coupling remains sufficiently strong to extract an effective Debye temperature (in agreement with the neutron scattering) as noted above and elsewhere [10].

The integrated intensity of the <010> x-ray peak does not show a clear change in slope at 160 K and is consistent with the high temperature value of the Debye temperature of 250 K [6]. This suggests that the electron cloud fluctuations normal to the film (but not necessarily in-plane) are generally weak, except near the transition temperature. Large, incoherent charge fluctuations are certainly expected in the vicinity of a phase transition from Landau theory [16]. There is no reason why such fluctuations cannot occur on a length scale so small that there is little influence on the generally excellent insulating properties of this P(VDF-TrEF) copolymer material. Orbital fluctuations can not be observed in neutron diffraction or EELS measurements.

The loss in intensity and the increase in FWHM at higher temperatures observed in EELS in Figure 3, are the expected behavior for the dipole active phonon modes. As the phonon population increases with temperature, the inelastic peaks broaden and decrease in amplitude. These particular dipole active modes are mainly in the surface and they indicate the intra-chain dipole alignment with respect to the surface normal. There are two distinct changes in the dipole EELS mode intensity and FWHM dependence with temperature. One occurs at low temperature, around 150 K and the other at approximately 315 K. The latter corresponds to the surface ferroelectric phase [9]. The jump of the FWHM and peak intensity in EELS occurs at the same temperature as the stiffening transition observed with neutron and X-ray diffraction at 160-200

K. The dipole active phonon modes studied in electron energy loss spectroscopy are very different than the inter-chain modes studied in neutron diffraction. There is no *a priori* reason that the temperature dependence should be the same, unless the transition temperature (160 K) drastically changes all acoustic and optical phonon modes or, there are two separate transitions occurring at the same temperature. We have no evidence that the dipole active phonon modes are completely decoupled from the other normal phonon modes, intra- or inter-chains. We propose that the changes observed in the dipole active phonon modes at low temperatures are not necessarily the driving mechanism for the stiffening transition that occurs in the bulk at 160 K, but a spectator to the changes in local electron-phonon coupling. A complete assignment of the phonon modes as a function of temperature can be undertaken using inelastic neutron diffraction which, in conjunction with careful in-plane dielectric measurements may provide insight to the extent electron-phonon coupling influences the ferroelectric properties of the P(VDF-TrFE, 70:30) copolymers.

In conclusion, we have found evidence for a change in electron-phonon coupling across the lattice stiffening transition at 160 K. Using temperature dependent neutron diffraction and photoemission measurement we have obtained the same value for the effective bulk Debye temperature of 48 K, indicating a relatively soft lattice above 160 K, adequate for a crystalline polymer. Below this temperature the stiffness of the lattice increases five times in the normal direction, but the coherence between polymer chains reaches a minimum value. Also, the electronic band structure shifts in binding energy, increasing the insulating properties of the material. The polymer chains at low temperatures are frozen in a distorted state, which affects the electronic bands differently than at higher temperatures, above 160 K.

References

[1] T.E. Felter, R.A. Barker, P.J. Estrup, Phys.Rev. Lett. 38, 1138 (1977); M.K. Debe and D. A. King, J. Phys. C 10, L303 (1977)

[2] I. S. Elfimov, V. I. Anisimov, and G. A. Sawatzky, Phys. Rev. Lett. 82, 4264 (1999)

[3] Minoru Nohara *et al.*, Phys. Rev. B 52, 570 (1995)

[4] F. Zwick *et al.*, Phys. Rev. Lett. 79, 3982 (1997)

[5] F. Zwick *et al.*, Phys. Rev. Lett. 81, 2974 (1998)

[6] C. N. Borca *et al.*, Phys. Rev. Lett. 83, 4562 (1999)

[7] S. Palto *et al.*, Ferro. Lett. 19, 65 (1995); A. Sorokin, S. Palto, L. Blinov, V. Fridkin, and S. Yudin, Mol. Mater. 6, 61 (1996)

[8] S. Ducharme *et al.*, Phys. Rev. B57, 25 (1998)

[9] Jaewu Choi *et al.*, Phys. Rev. Lett. 80, 1328 (1998)

[10] C. N. Borca *et al.*, Appl. Phys. Lett. 74, 347 (1999)

[11] Jaewu Choi, S.-J. Tang, P.T. Sprunger, P.A. Dowben, Stephen Ducharme, Jens Braun, E. W. Plummer, V.M. Fridkin, A. V. Sorokin, S. P. Palto, N. Petukhova, and S.G. Yudin, J. Phys.: Cond. Matter 12, 4735 (2000)

[12] J.E. Ortega, F.J. Himpsel, D. Li, and P.A. Dowben, Solid State Commun. 91, 807 (1994)

[13] Donqi Li, Jiandi Zhang, Sunwoo Lee, and P.A. Dowben, Phys. Rev. B 45, 11 876 (1992)

[14] J.E. Demuth, W.J. Thompson, N.J. DiNardo, and R. Imbihl, Phys. Rev. Lett. 56, 1408 (1986); M. Alonso, R. Cimino, and K. Horn, Phys. Rev. Lett. 64, 1947 (1990)

[15] T. Balasubramanian, P.-A. Glans, and L.I. Johansson, Phys. Rev. B 61, 12 709 (2000)

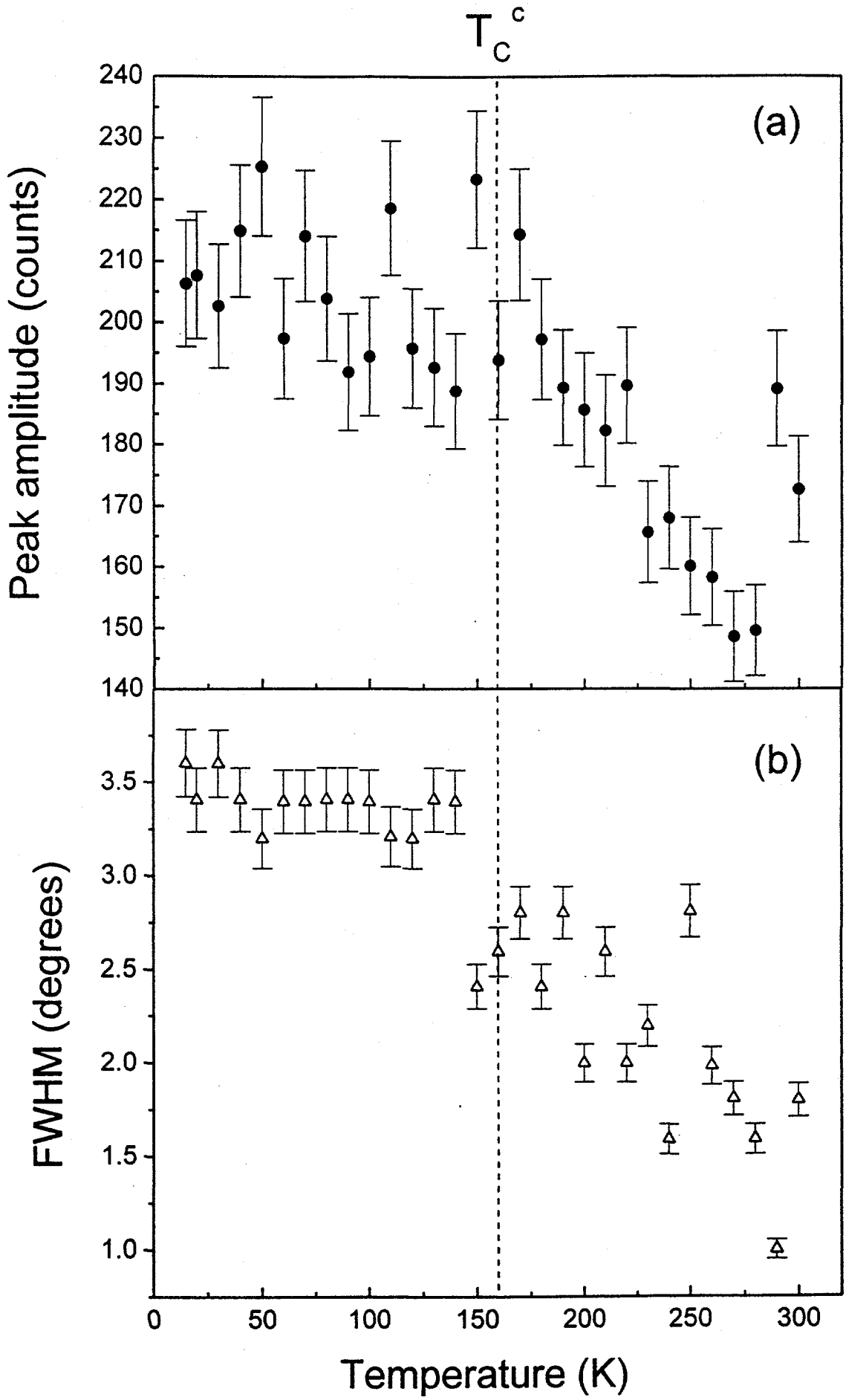
[16] L.D. Landau and E.M. Lifshitz, Statistical Physics, Course of Theoretical Physics Vol. 5 (Pergamon Press, New York, 1969)

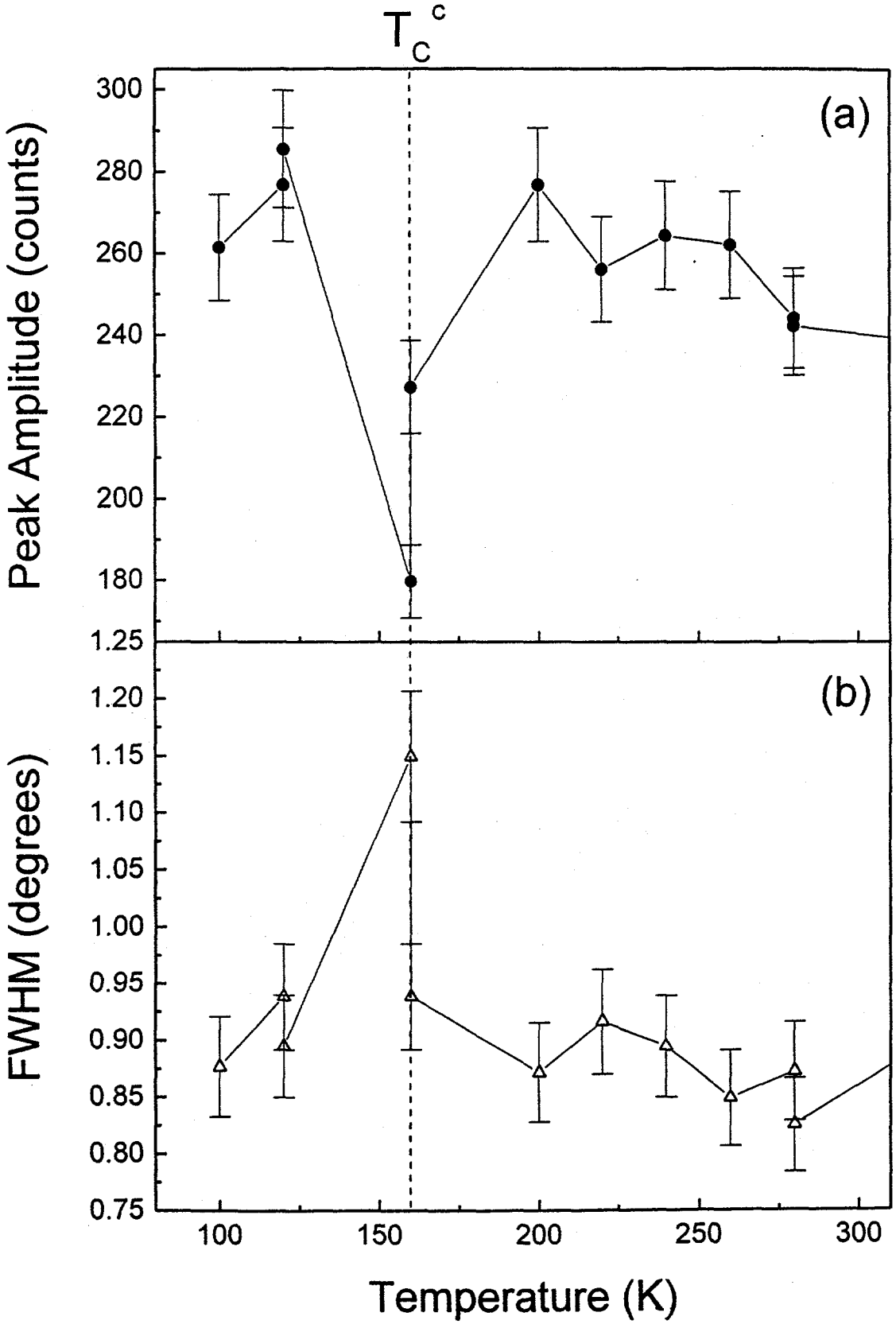
Figure Captions

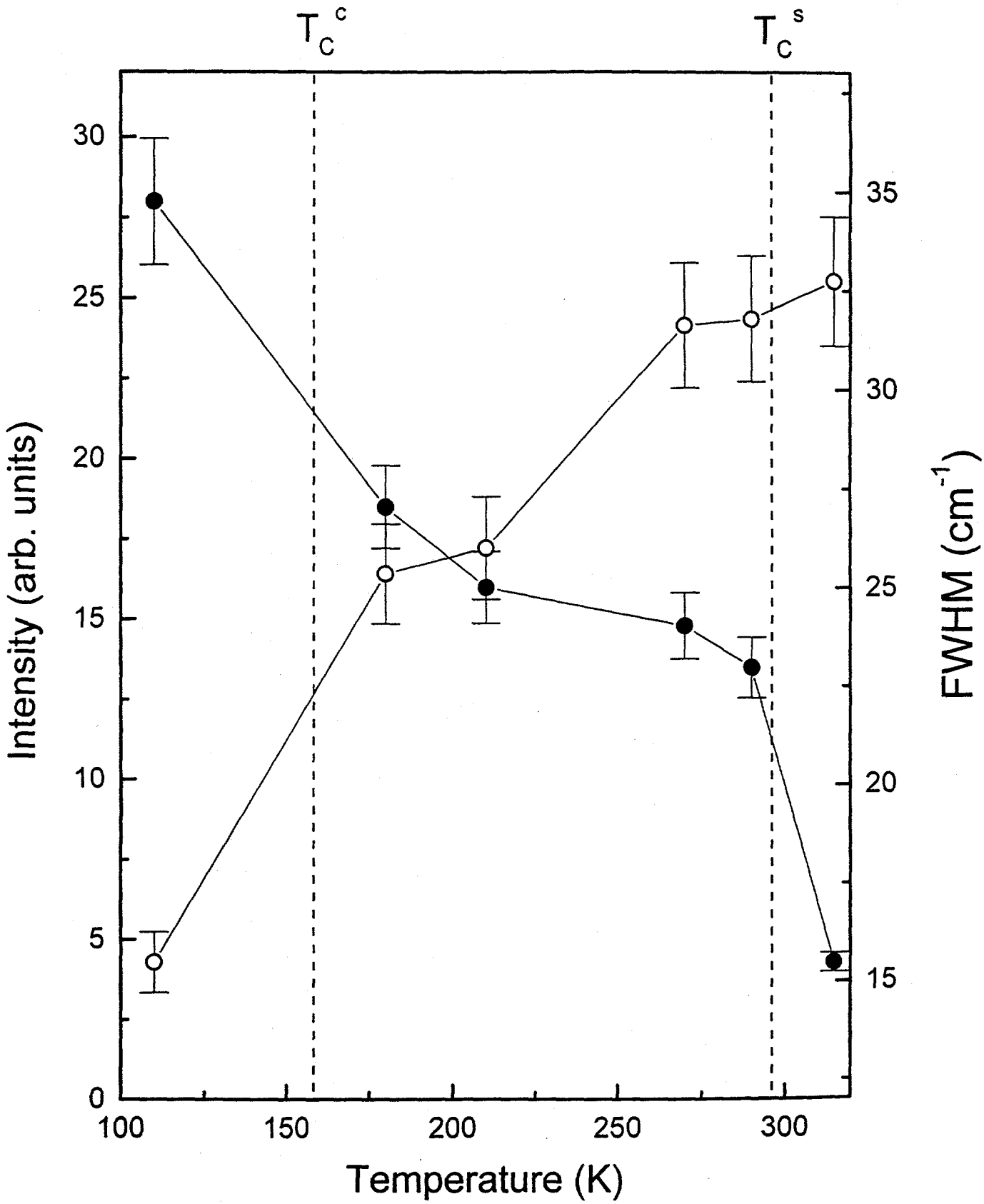
Figure 1. Neutron diffraction peak amplitude (a) and FWHM (b) as a function of temperature for a 100 monolayer thick film. The elastic diffraction peak corresponds to the interlayer spacing of $d \cong 4.5$ Å, in the <010> normal direction.

Figure 2. X-ray diffraction peak amplitude (a) and FWHM (b) as a fuction of temperature for a 5 monolayer thick sample. Dashed lines indicate the lattice stiffening transition ($T^c_C = 160$ K) and the ferroelectric-paraelectric surface phase transition ($T^s_C = 295$ K).

Figure 3. The intensity of the approximately 450 cm^{-1} dipole active optical mode (●) as a function of temperature is plotted along with the width of the approximately 1150 cm^{-1} dipole active optical phonon mode (○), as determined from EELS [11].


T_c^c
(a)
(b)
Peak amplitude (counts)
FWHM (degrees)
Temperature (K)
240
230
220
210
200
190
180
170
160
150
140
3.5
3.0
2.5
2.0
1.5
1.0
0
50
100
150
200
250
300


T_C^c
(a)
(b)
Peak Amplitude (counts)
FWHM (degrees)
Temperature (K)
300
280
260
240
220
200
180
1.25
1.20
1.15
1.10
1.05
1.00
0.95
0.90
0.85
0.80
0.75
100
150
200
250
300


T_C^c
T_C^s
Intensity (arb. units)
FWHM (cm^{-1})
Temperature (K)
0
5
10
15
20
25
30
15
20
25
30
35
100
150
200
250
300