

Low-temperature specific heat measurement of a ferroelectric copolymer film of vinylidene fluoride and trifluoroethylene

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The specific heat of a highly crystallized ferroelectric copolymer film of vinylidene fluoride (~ 80 mol%) and trifluoroethylene (~ 20 mol%) was measured over the previously unexplored temperature range from 3.7 to 8.5 K. The data show a dominant cubic temperature dependence, with only marginal evidence for a $T^{3/2}$ or a T^2 component. There is also no evidence for the discontinuity in slope that was observed in previous measurements of the pyroelectric coefficient of this material in the vicinity of 6 K. This difference is consistent with the supposition that thermal expansion is the dominant contributor to the pyroelectric coefficient in this temperature range. The specific heat data also show a rapid transition from the three-dimensional to one-dimensional Debye limits.

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I. Introduction

Prior measurements of the specific heat of the copolymer of vinylidene fluoride and trifluoroethylene (VDF-TrFE) do not extend below ~ 18 K.¹ The measurements reported here focused on that part of the unexplored temperature region where an anomaly was observed at ~ 6 K in the temperature dependence of the pyroelectric coefficient.^{2,3}

On a phenomenological basis, there are two mutually exclusive relationships between the specific heat and the pyroelectric coefficient that are potentially relevant at low temperatures. The choice of the appropriate one is determined by which of the two components of the pyroelectric coefficient is dominant. Those components are, the primary coefficient, which describes the surface charge response to heating of a clamped sample, and the secondary coefficient, due to the charge response caused by volume expansion of the sample.^{3,4}

When the primary pyroelectric coefficient is negative, as in most cases, and dominant, then Radebaugh used the third law of thermodynamics to predict that the pyroelectric coefficient and the specific heat would usually exhibit the same cubic temperature dependence as $T \rightarrow 0$.^{5,6} Although our data for the specific heat of the copolymer show the same cubic temperature dependence as that of the pyroelectric coefficient, from ~ 3.7 to 6 K, this agreement is probably coincidental.² In addition to the comparatively high temperatures of the data, there is also evidence from room-temperature measurements that the secondary pyroelectric coefficient is dominant for this copolymer.^{3,4}

An alternative relationship exists between the specific heat and the pyroelectric coefficient when the secondary component of the latter is dominant. This is because the temperature dependence of the secondary pyroelectric coefficient is typically determined by the thermal expansion coefficient α , which is in turn related to the specific heat c by the Grüneisen equation⁷⁻⁹

$$\alpha = \frac{1}{3} \frac{\rho}{\kappa} c \gamma, \quad (1)$$

where ρ is the density, κ is the bulk modulus, and γ is the Grüneisen coefficient.

The phenomenological basis for the Grüneisen relation is the assertion that the fractional change in frequency of each normal mode, n , is proportional to its fractional change in volume, with a proportionality constant, $-\gamma_n$.⁸ This condition is incorporated into the Helmholtz free energy, which is mini-

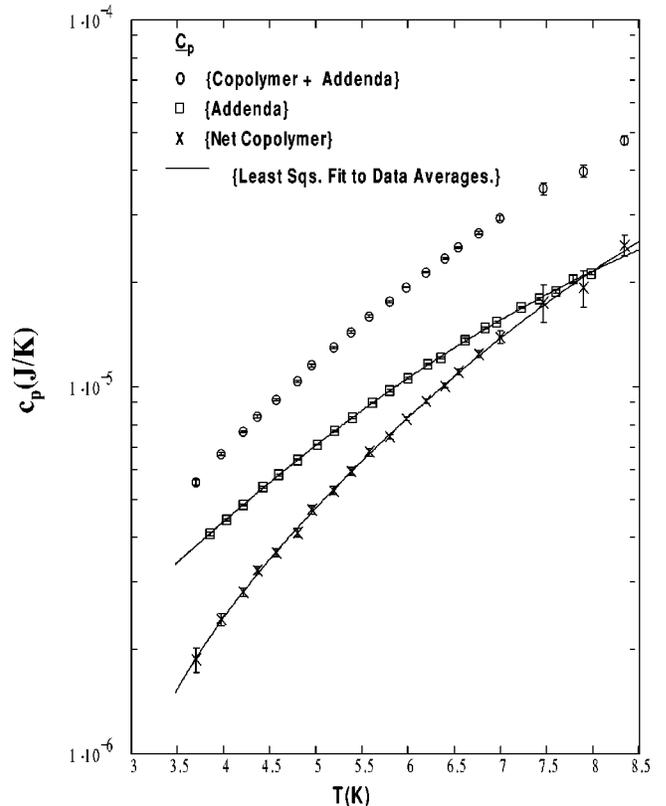


FIG. 1. A comparison of the measured components used to deduce the specific heat of a 0.62 mg sample of a copolymer of vinylidene fluoride and trifluoroethylene. The plots show the contributions from the sample plus the addenda, and the addenda, and the difference of the two. The vertical bars denote the $\pm \sigma$ range of statistical errors about the mean values.

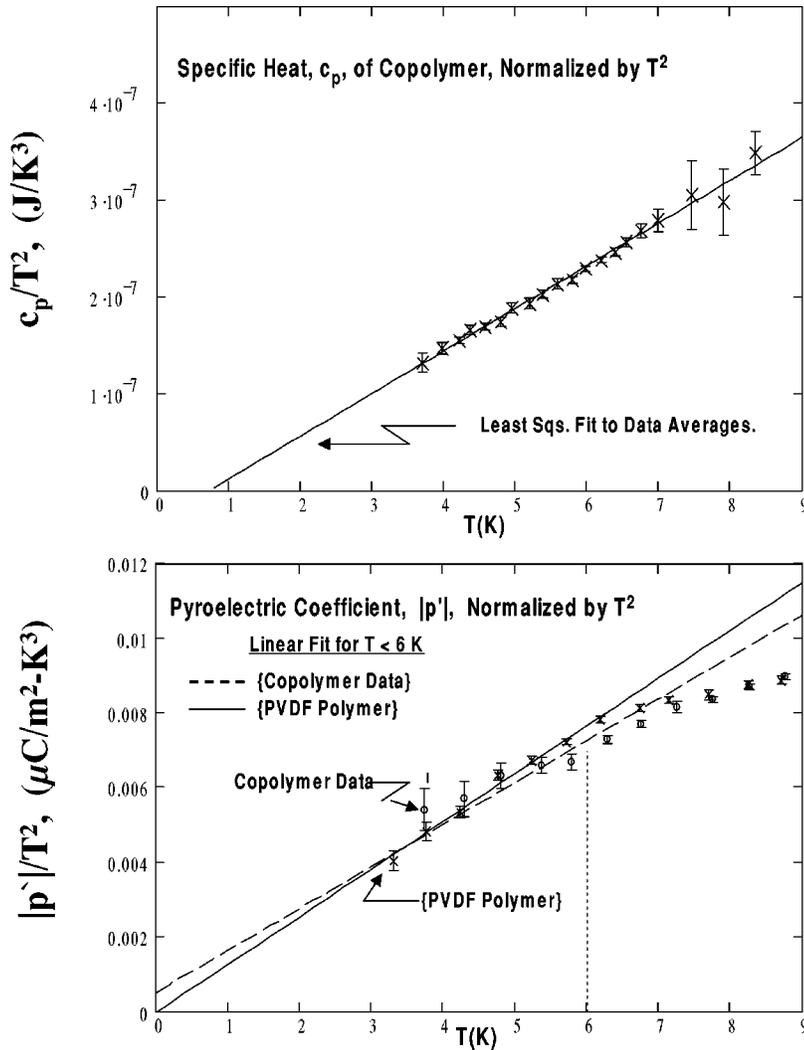


FIG. 2. Plots of the net specific heat and the pyroelectric coefficient, after normalizing with T^2 . Measurements of the pyroelectric coefficient for the copolymer are from Ref. 2, and for the related polymer (PVDF) are from Ref. 3.

mized to obtain an equation relating the fractional change in volume to the total internal energy. Differentiation with respect to temperature then yields the Grüneisen relation shown in Eq. (1), where γ represents a weighted mean of all the γ_n , with a weighting function c_n equal to the contribution to the specific heat from each normal mode. The overall specific heat c , in Eq. (1), represents the sum of contributions from all modes.^{8,9} It should technically be evaluated at constant volume, but it is customary to neglect the small difference between c_v and c_p at low temperature.

In an idealized situation in which all normal modes have the same value of γ_n , the temperature dependence of α and c are identical. In general, however, different modes are activated at different temperatures and exhibit characteristic differences in γ_n , which reflect distinctive types of dynamical behavior, such as longitudinal versus transverse oscillations. There are also differences among the γ_n coefficients for crystalline versus amorphous polymers.

The composite Grüneisen coefficient γ is a measure of the asymmetry of the binding potentials, whereas the specific heat c measures the density of thermal excitations.⁷ This asymmetry is directly related to thermal expansion, which is in fact zero for a perfectly symmetric potential. The van der

Waals potentials, provide the dominant forces between polymer chains at temperatures below ~ 2 K. The shape of these interchain potentials grow more asymmetric with increasing temperature, and produce corresponding increases in the Grüneisen coefficient. Intrachain interactions, due to comparatively symmetric covalent potentials, become dominant as temperatures increase above ~ 10 K, and they decrease the Grüneisen coefficient.

Specifically, several distinctive and relevant characteristics survive the complexity of possible contributions to γ , for amorphous and crystalline polymers over the temperature range of the measurements presented here. Note that the fractional crystalline content of our copolymer sample was ~ 0.77 . For amorphous polymers, the Grüneisen coefficient exhibits a broad peak at ~ 8 K which is several times larger than the comparatively flat profile, from ~ 1 K to ~ 15 K, in crystalline polymers.⁷ At the lower end of this temperature range, the Grüneisen coefficient for amorphous polymers falls rapidly below that for crystalline polymers, due to the onset of tunneling transitions which contribute to the specific heat of the former but not significantly to their thermal expansion. As temperatures increase above ~ 12 K, the values of γ for both amorphous and crystalline polymers gradually converge to approximately the same value.⁷

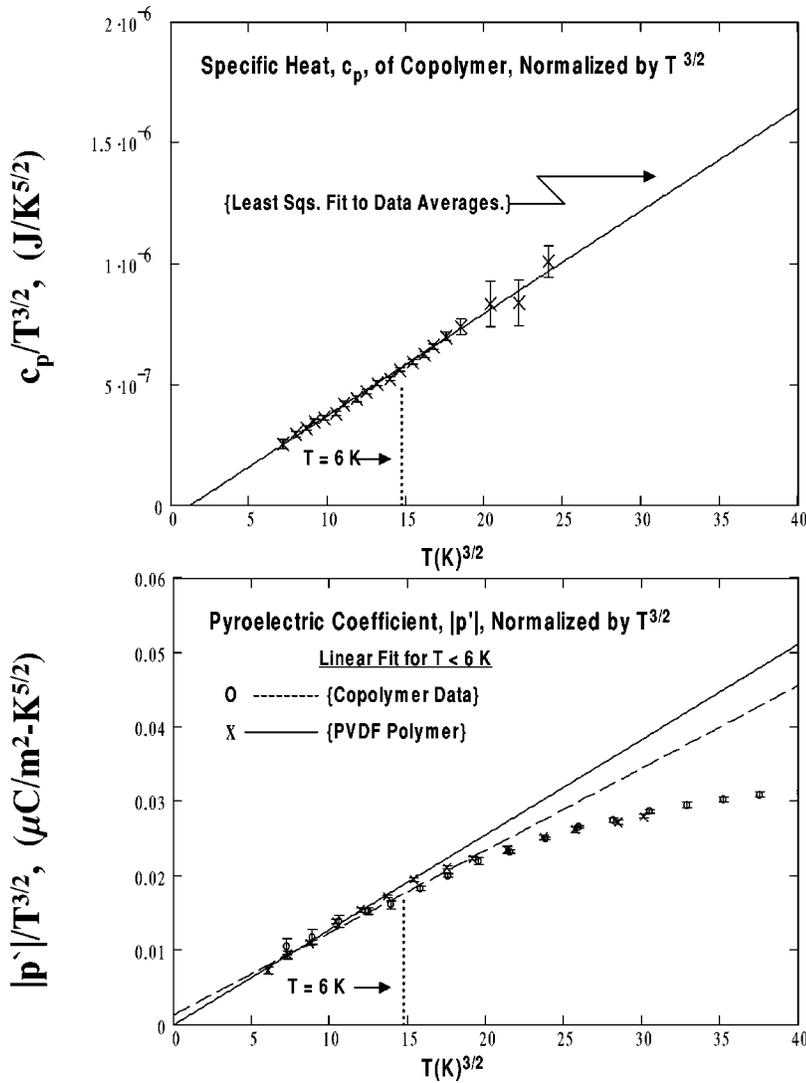


FIG. 3. Plots of the net specific heat and the pyroelectric coefficient, after normalizing with $T^{3/2}$. Measurements of the pyroelectric coefficient for the copolymer are from Ref. 2 and for the related polymer (PVDF) are from Ref. 3.

For temperatures below ~ 20 K, pure crystalline polymers usually exhibit the cubic temperature dependence for the specific heat predicted by the three-dimensional acoustic Debye theory.⁷ The thermal energy available in the lower part of this temperature range can only excite vibrational interactions between polymer chains, which are mediated by comparatively weak van der Waals forces. The associated phonons propagate isotropically in three dimensions, because their long wavelengths cannot resolve the morphological structure of the polymers. Thermal fluctuations in the upper part of this temperature range preferentially excite vibrations along the polymer chains, in the form of stretching and longitudinal components of bending modes. These motions are typically mediated by valence forces. The associated specific heats in both regimes are often in qualitative agreement with the Tarasov theory,¹⁰⁻¹² which provides a smooth transition between them via a linear combination of one-dimensional and three-dimensional Debye functions.

Vibrational motions associated with the transverse components of bending modes can also propagate in three dimensions at low temperatures. The corresponding density of states yield a $T^{3/2}$ temperature dependence for the specific heat.⁷

The specific heat is typically larger for amorphous than for crystalline polymers in the Debye regime, because the mean phonon velocity is smaller in amorphous media. Amorphous polymers often exhibit a deviant $T^{3.5}$ temperature dependence for their specific heat, which is sometimes attributed to localized vibrations of small molecular units.⁷ The complex behavior of amorphous polymers may compromise models based on phonon propagation, due to short lifetimes associated with conversion processes between stretching and bending modes.^{7,13} The rationale for neglecting these issues here is that the small amorphous content of our sample, $\sim 23\%$, did not produce a detectable deviation from the T^3 dependence. It may, however, be a primary source of the anomaly in the temperature dependence of the pyroelectric coefficient that was observed for this substance.²

II. Measurement Procedures

A. The sample and apparatus

The 10μ thickness of the copolymer sample was chosen to be the same as that previously used to measure the pyroelectric coefficient.² The sample weighed 0.62 mg, and con-

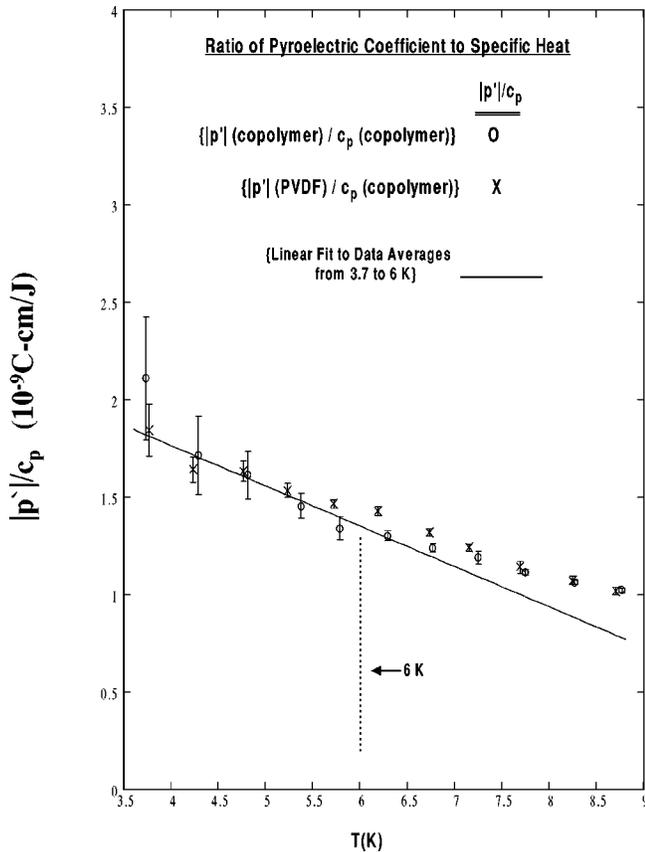


FIG. 4. Plots of the ratios of the pyroelectric coefficient divided by the specific heat. Measurements of the pyroelectric coefficient for the copolymer are from Ref. 2 and for the related polymer (PVDF) are from Ref. 3.

sisted of (~ 80 mol%) vinylidene fluoride (VF_2 , or VDF) and (~ 20 mol%) trifluoroethylene (VF_3 , or TrFE). It was provided without metallic backings from measurement specialties.¹⁴ A minute layer of silicon vacuum grease was used to attach the copolymer film to one side of a $125\text{-}\mu$ -thick wafer of alumina. This copolymer is a well-established ferroelectric, with a mean (heating and cooling) Curie transition temperature of ~ 400 K.¹⁵

The monomers for the two primary constituents of the copolymer studied here, are CH_2CF_2 and CF_2CHF , which, respectively, represent vinylidene fluoride and trifluoroethylene. Their basic structures are similar, and covalent bonds between carbon and fluorine atoms are the dominant source of their electric dipole moments. The trifluoroethylene units are randomly distributed in the polymer chain, and steric conflicts due to replacement of a hydrogen atom by a larger fluorine atom, cause the copolymer to crystallize directly into the β phase. This phase has a net polarization per unit cell, which must be artificially induced in polyvinylidene fluoride (PVDF) by mechanical stretching.⁴

The calorimetry data were reduced with the algorithm developed by Hwang *et al.*,¹⁸ as modified for our configuration in which a Cernox thermometer also served as a heater. The overall noise in quiescent temperature readings was $\approx \pm 1$ mK at ~ 6 K. Additional details about the cryostat and the data reduction are described in Ref. 17.

B. The measured specific heat of the copolymer

The data summarized in Fig. 1, were averaged over bin sizes of 200 mK, for temperatures below 7 K, and 400 mK above that temperature due to poorer statistics there. The statistical errors associated with the subtraction of the addenda were reduced to satisfactory levels by signal averaging over data collection runs of ~ 96 h duration.

The vertical error bars in Fig. 1 represent only statistical uncertainties deduced from the data, and do not include systematic errors. Two additional sources of such errors are the temperature calibration and the weight of the sample.

The temperature calibration was rechecked after completion of all the measurements. The results of the recheck showed that our previous calibration was offset by 200 mK. This correction was applied to all the data presented here.¹⁷

The mechanical and electronic balances used for weighing the samples had an accuracy of $10\ \mu\text{g}$ but inaccuracies during weighing ranged up to $100\ \mu\text{g}$. Estimates of the impacts of these uncertainties indicate that they do not cause shifts larger than the stated range of statistical uncertainties. This is confirmed by our measurements of the specific heat of copper, using the same apparatus and analysis procedures.¹⁷

C. Comparisons of linearized plots of the specific heat and the pyroelectric constant

The data for the net specific heat, originally plotted in Fig. 1, are replotted in the upper panel of Fig. 2 with a normalization of T^2 . If the specific heat c_p consists of a sum of T^3 and T^2 components, then this normalization would yield a linearized temperature dependence of

$$\frac{c_p}{T^2} = aT + b, \quad (2)$$

where a and b are constants.

Note that the intercept b would be zero if there were no T^2 component. Although the least-squares fit to the normalized data in the upper panel of Fig. 2 is consistent with a small T^2 component, the latitude of the statistical error bars would also permit a zero intercept. Nevertheless, a straight line is obviously a good fit to these data, which is indicative of a dominant T^3 component.

The lower panel in Fig. 2 summarizes the result of a T^2 normalization to previously measured data for the pyroelectric coefficient.^{2,3} Note the discontinuity in the slope of these data in the vicinity of 6 K. That anomaly was a prime motivator for the specific heat measurements presented here. The absence of a similar anomaly, in the data for the specific heat, is consistent with a dominant secondary component to the pyroelectric coefficient whose temperature dependence is determined by the thermal-expansion coefficient.³

The data plotted in Fig. 3 show the results of changing the previous normalization from T^2 to $T^{3/2}$. The linearized fits, below ~ 6 K, exhibit intercepts that are approximately zero, which is again consistent with a dominant T^3 component and negligible contributions from $T^{3/2}$. The anomaly observed in

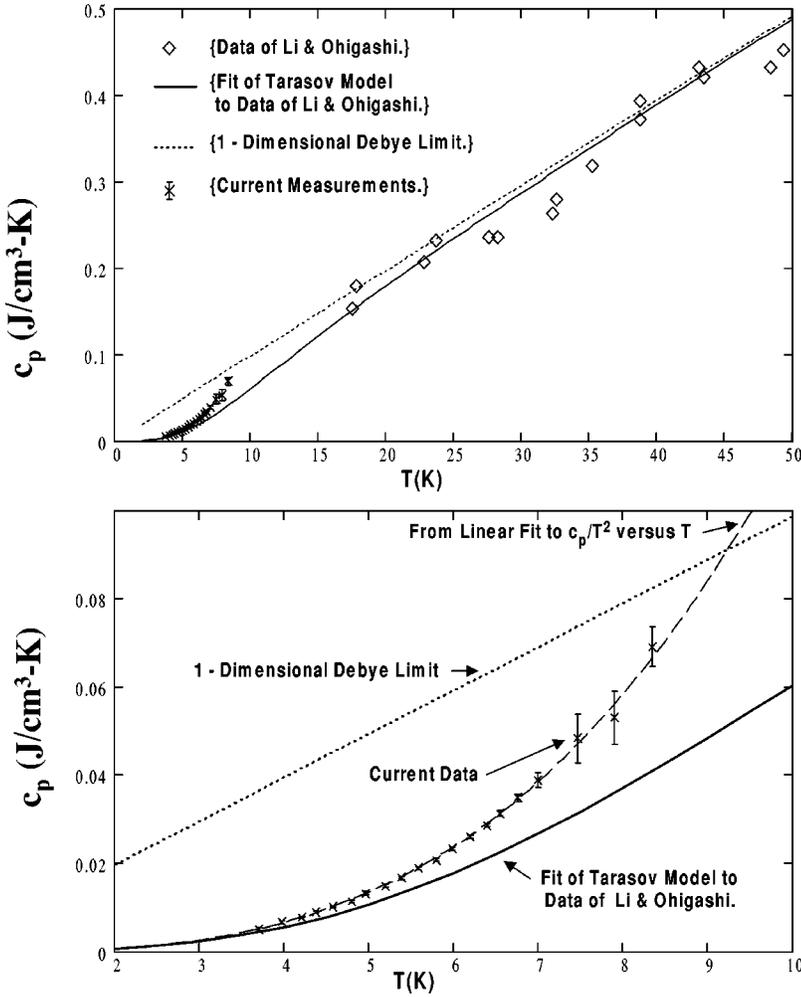


FIG. 5. Comparisons of our specific heat data with extrapolations of a fit to the Tarasov model (Ref. 10) by Li *et al.* (Ref. 1), of their data above ~ 18 K.

the slope of the pyroelectric coefficient is again missing in the linearized plot of the specific heat data.

The data in Fig. 4 utilize the previously displayed data to generate plots of the ratio of pyroelectric coefficient divided by the specific heat. All the ratios plotted in this figure use the current data presented here for the specific heat of the copolymer, but there are two different alternative sets of data for the pyroelectric coefficient. One is for the copolymer studied here and the other is for a related polymer (polyvinylidene fluoride), whose polarization phase is induced by mechanical stretching. The ratios for both sets of data are essentially the same for temperatures above ~ 4 K. The upward trend in the values of these ratios, as the temperature decreases, is consistent with the plot of similar ratios by Li and Ohigashi¹ for temperatures above ~ 10 K. The small but distinct deviation in the slope of the data in Fig. 4 reflects the observed behavior of the pyroelectric coefficient. If our conjecture is correct, then the ratios plotted in this figure reflect the temperature dependence of the Grüneisen coefficient γ in Eq. (1).

D. Comparisons with the Tarasov model

The data for the net specific heat of the copolymer are replotted in Fig. 5 to facilitate comparisons with data of

Li *et al.*,¹ As the temperature range of our data sets do not overlap, we used the Tarasov model to extrapolate the Li data below ~ 18 K. This Model utilizes a linear combination of Debye functions to approximate the transition from three-dimensional vibrations at very low temperatures, to predominantly one-dimensional vibrations at higher temperatures.^{1,10-12} The expression for the specific heat is

$$c = N_d k \left(D_1 \left(\frac{\Theta_1}{T} \right) - \frac{\Theta_3}{\Theta_1} \left[D_1 \left(\frac{\Theta_3}{T} \right) - D_3 \left(\frac{\Theta_3}{T} \right) \right] \right), \quad (3)$$

where the one-dimensional and the three-dimensional Debye functions are, respectively, defined as

$$D_1 \left(\frac{\Theta}{T} \right) = 3.0 \left(\frac{T}{\Theta} \right) \int_0^{\Theta/T} \left(\frac{x^2 e^x}{(e^x - 1)^2} \right) dx, \quad (4)$$

$$D_3 \left(\frac{\Theta}{T} \right) = 9.0 \left(\frac{T}{\Theta} \right)^3 \int_0^{\Theta/T} \left(\frac{x^4 e^x}{(e^x - 1)^2} \right) dx. \quad (5)$$

The parameters used by Li *et al.*¹ to fit their data above 18 K are $\Theta_1 = 460$ K, $\Theta_3 = 52$ K, and $N_d k = 0.46$ J/cm³K, where k represents the Boltzmann constant. They were used to generate the lower solid curves in Fig. 5. The authors Li

et al.,¹ note that their value for the parameter N_{dk} corresponds to ≈ 3.6 repeat units per unit cell of the copolymer. They also note the plausibility of this number if a unit cell is assumed to contain an average of two units of CF_2 , and 1.5 units of CH_2 , and 0.5 units of CHF. Contributions from optical transitions are assumed to be negligible at temperatures below ~ 50 K.

As shown in Fig. 5, our specific heat data below ~ 4 K, merge smoothly with the extrapolated fit to the data of Li *et al.*¹ This is consistent with the expectation of a predominance of three-dimensional phonon propagation in polymers at very low temperatures. The plots of our data in this figure also show evidence of an expected shift toward the one-dimensional Debye limit with increasing temperature, but this transition in our data deviates significantly from the Tarasov prediction. Additional measurements are needed to cover the gap in the data for specific heat from ~ 8 K to ~ 20 K. This difference is accentuated by the smooth curve through our data points, which was deduced from the linearized fit to these data in Fig. 2.

III. Summary and Conclusions

The specific heat of a $10\text{-}\mu$ -thick film of a copolymer consisting of vinylidene fluoride and trifluoroethylene was measured over the previously unexplored range from 3.7 to 8.5 K. The data are consistent with a dominant cubic temperature dependence, without anomalies, over the entire measured range. There is only marginal evidence for either a T^2 or a $T^{3/2}$ component.

The focus on this temperature regime was motivated by prior detection of a distinct break in the slope of the pyroelectric coefficient at ~ 6 K for a similar copolymer,² and also for pure polyvinylidene fluoride.³ An explanation for the absence of similar anomalies in our specific heat measurements may be provided by the Grüneisen relation, if the dominant contribution to the pyroelectric coefficient is from thermal expansion, which is known as the secondary contri-

bution. The anomaly previously detected in the pyroelectric coefficient, could therefore be absorbed into the Grüneisen coefficient and not the specific heat. The assumption of a large amorphous contribution to this anomaly, might be tested by repeating both sets of measurements with a sample containing a significantly different amorphous content. In this approximation, the ratios of the pyroelectric coefficient to the specific heat yield the temperature dependence of the Grüneisen coefficient.

It is of interest to note that the specific heat of crystalline polyethylene, consisting of monomer units of CH_2 , also has a pure cubic dependence below ~ 6 K.^{19,20} This confirms the utility of the Debye approximation at temperatures where long phonon wavelengths are insensitive to smaller scale details of chemical composition.

The temperature dependence of the measured specific heat follows the expected shift with increasing temperature from the three-dimensional to one-dimensional Debye limits set by an extrapolation of the fit to the Tarasov model by Li and Ohigashi¹ for their data above ~ 18 K. Our data, however, exhibit a transition between these limits which is more rapid than that indicated by this model over the measured temperature range. Additional measurements are needed to cover the gap in the data from ~ 8 K to ~ 20 K, in order to clarify the eventual merger of the specific heat data with the one-dimensional Debye limit.

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