properties,[14] and experimental evidence has been cited as tentative confirmation.[7] However, a critical and definitive test of this suggestion, such as that presented in the present Letter for interstitial boron, has yet to be successfully accomplished. Work is in progress in our laboratory to attempt this more difficult test as well.

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Electric Field Dependence of Crystallinity in Poly(Vinylidene Fluoride)

R. G. Kepler, R. A. Anderson, and R. R. Lagasse
Sandia National Laboratories, Albuquerque, New Mexico 87185

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It is shown that the crystallinity of poled films of poly(vinylidene fluoride) can be changed by the application of an electric field. This is the first time that electric-field–induced changes of crystallinity in a polymer have been reported, and this observation confirms the hypothesis that reversible changes in crystallinity with temperature contribute significantly to the pyroelectric effect in poly(vinylidene fluoride).

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Recently, it has been recognized that poly(vinylidene fluoride) and some vinylidene fluoride copolymers are ferroelectric. This discovery has stimulated a large amount of research since ferroelectricity had not been observed previously in polymers.[1-3] Much of this work has been devoted to explaining the origin and the magnitude of the pyroelectric effect.

In this paper, we report the observation of electric-field–induced changes of crystallinity in poly(vinylidene fluoride). We show that this observation confirms our earlier speculation[4,5] that a reversible temperature dependence of the crystallinity contributes significantly to the pyroelectric effect in poly(vinylidene fluoride). The fact that reversible changes in crystallinity can contribute to the pyroelectric effect has not been recognized previously, nor have electric-field–induced changes in crystallinity been observed.

Poly(vinylidene fluoride) is a crystalline polymer with a crystallinity χ_c of about 0.5; that is, about half of the molecules are in the crystalline phase. In the planar zigzag configuration, the β phase, the crystalline region is strongly polar. If the polarization axes of the crystalline regions are aligned by the application of a high electric field, referred to as a poling process, the polarization P of a sample is $\chi_c P_c$ where P_c is the polarization of the crystalline phase. Therefore, pyroelectricity, the change in sample polarization caused by a change in temperature, can arise not only from changes in the temperature dependence of the polarization of the crystalline phase but also from the temperature dependence of the crystallinity.

In earlier work, we found that we were unable to account for all the observed pyroelectricity on the basis of traditional primary and secondary pyroelectricity and speculated at that time that reversible changes in crystallinity might be providing the unaccounted-for pyroelectricity.[4] More recently, we showed that the time dependence of the appearance of the pyroelectric change is consistent with this hypothesis.[5] Dvey-Aharon, Sluckin, and Taylor[6] have recently considered a model in which reversible changes in crystallinity are allowed.

Additional support for this hypothesis is given by the report that the crystallinity of polyethylene changes from 67% at 25 °C to 57% at 110 °C.[7] If a change in crystallinity of the same order of magnitude occurs in poly(vinylidene fluoride), this effect could easily account for a large fraction of the observed pyroelectricity.

Recently, we recognized that this hypothesis predicts that the crystallinity of poled films of poly(vinylidene fluoride) will be a function of an applied electric field. The argument is the same as that used to derive the Clausius-Clapeyron equation, and it is easy to show that the change in melting temperature, ΔT_m, resulting from a change in the applied electric field ΔE is

$$\Delta T_m = (T/l)\vec{\mathrm{P}}_c \cdot \Delta\vec{\mathrm{E}},$$

where l is the latent heat of melting. If it is assumed that the fraction of the pyroelectric coefficient p which results from reversible changes in crystallinity is κ, then

$$\Delta\chi_c/\Delta T = \kappa p/P_c.$$

If it is also assumed that a change in the melting temperature ΔT_m caused by an electric field results in the same amount of melting or crystallization at constant temperature as would result from an actual change in temperature of the same amount but of the opposite sign, then

$$\frac{\Delta\chi_c}{\Delta E} = -\frac{\Delta\chi_c}{\Delta T}\frac{\Delta T_m}{\Delta E} = -\frac{\kappa p T}{l} \tag{1}$$

if the applied electric field is parallel to the polarization.

In order to test this prediction, we have measured the change in crystallinity in 30-μm-thick films of poled poly(vinylidene fluoride) β-phase films (Piezofilm from Kureha) by measuring the change in intensity of x rays diffracted from the 200 and 110 planes when an electric field is applied. The films were glued to an aluminum plate which served as one electrode. A thin evaporated aluminum film served as the other electrode, and the incident and diffracted x-ray beams passed through this electrode. The intensity of x rays diffracted from films of poly(vinylidene fluoride) as a function of film orientation and the orientation distribution of crystallites in the films have been discussed previously.[8]

The intensity of the diffracted x-ray beam was obtained by integrating the total number of x-ray photons counted during an automatic scan of 2θ at $\frac{1}{2}°$ min^{-1} from 19.25° to 21.75°. No attempt was made to subtract the background counts since they contributed only a small fraction of the total counts. The width of the diffraction peak at half maximum intensity was about 1.1°.

The change in intensity induced by a given electric field was determined by taking the average of twelve measurements of the change resulting from the application or removal of the electric field. The intensity was first measured with no voltage applied. Subsequent measurements of intensity were obtained at voltages applied according to the following sequence: positive, zero, negative, zero. This sequence was repeated until thirteen measurements of intensity were acquired, from which the twelve intensity changes were calculated. The percentage change in intensity as a function of applied voltage for one sample is shown in Fig. 1.

The average change in intensity with applied electric field for a given sample was found by fitting a least-squares line, which was constrained to pass through the origin. Three samples were measured, and the average field dependence of the crystallinity was found to be $(1.8 \pm 0.2)\times10^{-10}$ (V/m)$^{-1}$ where the error quoted is the estimated error in the mean obtained from the experimental data.

In order to check for spurious effects, we ran a control experiment on an unpoled, 50-μm-thick, β-phase film. The application of an electric field to an unpoled sample should not result in any change in crystallinity, and no effect was observed, even though fields up to 4×10^7 V/m were applied. A least-squares fit to the experimental data on one sample yielded a coefficient of $(-0.43 \pm 1.5)\times10^{-11}$ (V/m)$^{-1}$. This is 40 times smaller and opposite in sign to that obtained with the poled film.

It has occurred to us that electric-field–induced changes in the amplitude of libration of molecules

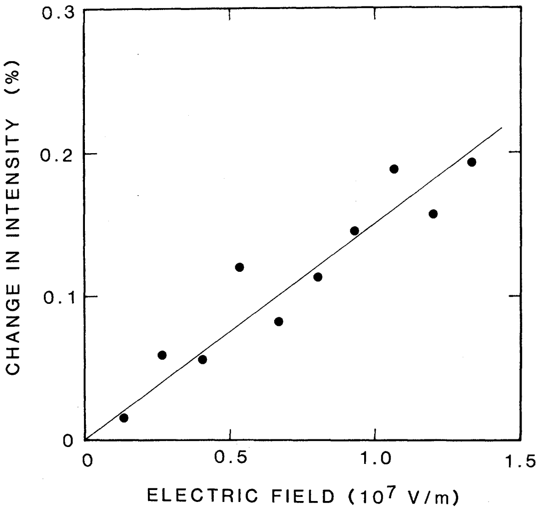

FIG. 1. The change in intensity of the diffracted x-ray beam as a function of the applied electric field as observed for one sample: The solid line is the least-squares line defined by the data.

in the crystalline phase might also cause the effect observed. In order to distinguish between this hypothesis and that of changes in crystallinity, we have made some measurements of the temperature dependence of the effect observed. At −50 °C, which is below the glass transition temperature for poly(vinylidene fluoride), no effect of the electric field on the diffracted x-ray intensity could be observed. Only one sample was studied at low temperature, but for that sample, the change in diffracted x-ray intensity for 400 V at room temperature was found to be (0.15 ± 0.03)%. At −50°, the change was (−0.01 ± 0.03)% where the minus sign indicates a change opposite to the direction expected. At +50 °C, the change in intensity of the diffracted x rays caused by the application of an electric field was found to be about 50% larger than at room temperature for the three samples mentioned above.

These results are consistent with the reversible crystallinity hypothesis but inconsistent with an effect of the electric field on the amplitude of libration in the crystalline phase. Below the glass transition temperature (about −40 °C), it should not be possible to change the crystallinity, and it is reasonable to expect that the amount of reversible melting increases rapidly with increasing temperature as the experimental observations imply. On the other hand, any change in intensity due to an effect of the electric field on the amplitude of libration in the crystalline phase should be only linearly dependent on the absolute temperature according to a simple model that we have considered.

Predicting $\Delta\chi_c/\Delta E$ from Eq. (1) requires the latent heat of melting for the temperature at which the electric field is applied. A value for l at room temperature was estimated from the standard relation

$$l(T_2) = l(T_1) - \int_{T_2}^{T_1} (C_a - C_c)\,dT, \qquad (2)$$

where C_a and C_c are heat capacities of the liquid and crystal. The heat absorbed in melting the partially crystalline Piezofilm was found to be 53 J per gram of sample (13 cal g^{-1}). This measurement plus an assumed weight fraction crystallinity of 0.5 yielded $l(375\ \mathrm{K}) = 110$ J per gram of crystal (26 cal g^{-1}).[9] Heat-capacity measurements above the melting point were fitted by a linear function to determine C_a. C_c was computed by combining heat-capacity measurements below the melting point, the assumed $\chi_c = 0.5$, and the C_a function. With these input data, Eq. (2) yielded $l(298\ \mathrm{K}) = 55$ J g^{-1} (13 cal g^{-1}). This estimate does not account for the likelihood that crystals melting near 298 K probably have a higher defect concentration than the majority of crystals, which melt at 430–450 K. For this reason, l at room temperature is probably lower than the estimate.

With use of 55 J g^{-1} as the latent heat for melting at room temperature and with the assumption[4,5] that one-third of the pyroelectric effect at room temperature results from reversible changes in crystallinity, Eq. (1) predicts that the field dependence of crystallinity should be 2.8×10^{-11} $(\mathrm{V/m})^{-1}$ for a pyroelectric coefficient of -2.7×10^{-5} C m^{-2} K^{-1},[10] compared to the experimentally observed value, 1.8×10^{-10} $(\mathrm{V/m})^{-1}$. We speculate that this large discrepancy results from a large difference between the actual latent heat for melting and our estimate. Some discrepancy might also be accounted for by the fact that the polymer films are heterogeneous, and the dielectric constant (and perhaps the conductivity) of the amorphous phase is much larger than that of the crystalline phase. Depending on the morphology, the resulting field enhancement in the crystalline phase could account for up to a factor of 2 in the discrepancy.

In summary, we believe that our observations show that an electric field can change the crystallinity of β-phase poly(vinylidene fluoride). The magnitude of the change confirms the hypothesis that a reversible temperature dependence of the crystallinity accounts for a significant fraction of the pyroelectric coefficient.

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Optical Detection of Multiple-Trapping Relaxation in Disordered Crystalline Semiconductors

E. O. Göbel and W. Graudszus
Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany

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Relaxation of optically excited carriers within localized continuum states in heavily doped crystalline GaAs is directly observed by picosecond luminescence experiments. The relaxation within localized states takes place via thermally activated multiple trapping. Saturation of the relaxation is observed at high temperatures and for small trap densities. The results demonstrate that heavily doped crystalline semiconductors can serve as a simple model for amorphous materials.

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The physical description of amorphous semiconductors in relation to crystalline materials is one of the basic problems in modern solid-state physics.[1,2] One of the most striking effects peculiar to amorphous semiconductors is the occurrence of so-called dispersive transport.[3-8] The dispersive nature manifests itself in transient transport experiments as a decrease of the effective carrier mobility of the photoexcited carriers. Multiple-trapping relaxation within the localized electronic states has been suggested to explain this effect.[8-10]

In this paper we report the first observation of multiple-trapping relaxation in a heavily doped *crystalline* semiconductor. Heavy doping in crystalline semiconductors produces quasilocalized electronic continuum states below the actual band gap of the pure material ("tail states").[11,12] These electronic states arise from the statistical distribution of the ionized impurity atoms. The density-of-states function in the highly doped crystalline semiconductors can be approximated by an exponential distribution for energies well below the band gap,[11,12] similar to amorphous materials. Heavily doped semiconductors therefore may serve as a model for disordered (amorphous) materials; however, the density of states within the tail-state region can be varied in a wide range by simply changing the doping concentration. Doped semiconductors hence provide the unique possibility to simulate a continuous transition from the crystalline to the amorphous state.

We have chosen Si-doped single-crystalline