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Enhancement of energy loss of fast electrons in a ferroelectric medium near the Curie temperature

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The temperature dependence of the energy loss of 624-keV electrons in ferroelectric barium titanate ($BaTiO_3$) and triglycine sulfate [$(CH_2NH_2COOH)_3\ H_2SO_4$] has been studied with the use of a single-gap magnetic spectrometer. The present measurements confirm the anomalous increase in energy loss of electrons near the Curie temperature T_C and indicate its dependence on (a) the magnitude of the dielectric anomaly at T_C, (b) the effect of a dc electric field larger than the coercive field, and (c) the application of an alternating electric field. Probable mechanisms for the origin of the observed phenomenon are discussed.

I. INTRODUCTION

The energy loss of high-energy electrons traversing a material medium takes place principally through ionization and excitation of the atoms and through bremsstrahlung radiation. These processes are almost independent of the temperature of the medium. However, it was recently observed by Lagare and Umakantha[1] that the energy loss measured as a function of temperature in a ferroelectric medium shows an anomalous increase of about 4% near the Curie temperature (T_C). In a second communication[2] they reported the measurement of the relative transmission of β particles through thick ferroelectric targets. The target thickness was chosen to be comparable to the range of β particles in that medium; and a small dip in the β transmission was observed near T_C. The physical origin of this phenomenon, however, remained unexplained. The present investigations involving the ferroelectrics barium titanate ($BaTiO_3$) and triglycine sulfate [$(CH_2NH_2COOH)_3H_2SO_4$] were undertaken with a view to study the dependence of the observed anomaly on the known dielectric properties of the material. In addition to repeating the previous measurements with higher energy resolution, better temperature stability and reduced γ background, the anomalous increase in energy loss has been measured in a number of samples of various thickness along different crystallographic directions. The effect of the application of a dc or high-frequency ac field was also studied in order to obtain a physical understanding of the problem.

It should be emphasized here that the microscopic mechanisms leading to ferroelectric ordering are quite different for the two substances chosen. Barium titanate (BT) is a "displacive" ferroelectric in which one of the transverse-optical- (TO) phonon branches softens at the wave vector $k \simeq 0$ near T_C. The resulting static atomic displacements in the low-symmetry phase leads to ferroelectric ordering. On the other hand, triglycine sulfate (TGS) is an "order-disorder" ferroelectric in which the "soft" collective excitations are unstable pseudospin waves rather than phonons. This brings out the importance of trying to relate the energy-loss anomaly to the macroscopically similar and temperature-dependent properties of the two types of ferroelectric media.

II. EXPERIMENTAL DETAILS

A single-gap magnetic spectrometer was used to focus the 624-keV internal conversion electrons from a 0.2-mCi ^{137}Cs source on the target under study. The target was shielded from the 662-keV γ rays emitted by the source by a 20-cm-thick lead wall. This is of particular importance since radiation damage effects have been observed in TGS even for a small dose of 30-keV x rays.[3] The electron beam size was about 5 mm in diameter at the target which was mounted on a special sample holder. The electrons transmitted through the target were detected by a Si(Li) detector cooled to 77 K having a 6-μm aluminized Mylar window and the whole assembly was enclosed in a chamber evacuated to about 10^{-2} Torr (Fig. 1). The detector was also shielded from the 662-keV γ rays from the source and its output was amplified by means of a charge sensitive preamplifier and a spectroscopy amplifier. The data was stored in a 512-channel analyzer. The integrated count rate was continuously monitored by a scaler to ensure the stability of the setup. The electron-beam intensity was typically $\sim 10^2$ counts sec^{-1} during the measurements.

The sample holder was a copper block with a central hole which would completely cut out any unfocused or stray electrons and also help attain thermal stability. Sample heating was accomplished by embedding within the copper block a length of nichrome wire wound on a ring-shaped mica strip and insulated by two other similar strips on either side. The temperature of the copper block was measured by an accurately calibrated Pt resistance

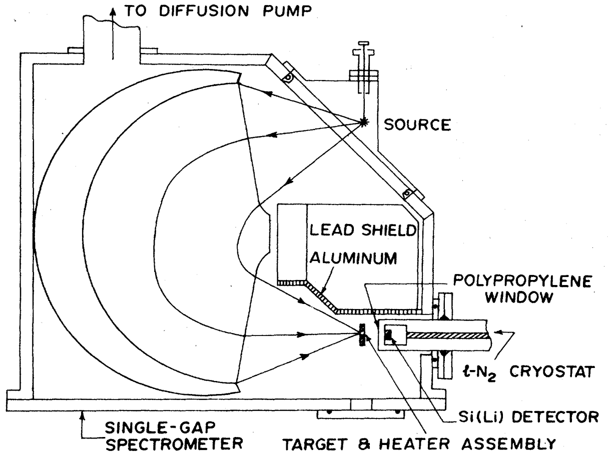

FIG. 1. Magnetic dispersion spectrometer used for electron-energy-loss measurements.

thermometer. Temperature stability of about ±0.1 °C was obtained using a temperature controller with an iron-Constantan thermocouple attached to the holder. The target (crystal) was held down from above by a small hollow copper cylinder thermally connected but electrically insulated from the main block through a boron-nitride disk. Such an arrangement permitted (a) the *in situ* measurement of the capacitance of the target, and (b) the application of a steady or an alternating voltage on the target. A VHF oscillator was used for applying high-frequency signals to the target.

The ferroelectric targets studied were TGS single crystals of different thickness cut normal to either the crystallographic *b* (ferroelectric) or *c* axes and BT single crystals cut normal to the *c* (ferroelectric) axis and polycrystalline pellets of BT. The target thickness between 0.1 and 0.5 mm were achieved for TGS by careful lapping with water and for BT by dipping in hot phosphoric acid and polishing with very fine alumina powder. A thickness uniformity of ±0.01 mm was achieved for targets of approximately 8 mm diameter. A thin layer of gold (20—30 $\mu g/cm^2$) evaporated onto the crystals formed the electrodes. The temperature dependence of the dielectric constant of the samples was accurately measured with an autobalance bridge.

While mounting the target in the holder a small gap was deliberately left in the path of incident electrons so as to transmit some of them without any energy loss. These electrons produced a narrow peak at the channel corresponding to the incident energy which was used as a reference for calculating energy shifts and to monitor the long-term stability of the spectrometer. Typically, this peak position shifted by less than ±0.2 keV during a complete set of scans while the full width at half maximum (FWHM) was around 5 keV. The target was covered with a thin (5.4 mg/cm^2) aluminum foil to achieve temperature uniformity over the sample. The temperature was allowed to stabilize for about an hour after the desired setting before starting data acquisition. The acquisition time at each temperature for a particular sample depended on the corresponding count rate and was usually between 1 to 2 h.

III. DATA ANALYSIS

The observed electron spectrum consists of a narrow peak corresponding to electrons suffering no energy loss and a broad asymmetric peak due to electrons suffering energy loss in the target. The relatively large width of the energy-loss peak is due to straggling in the target. The long tail of this curve on the low-energy end is due to the relatively infrequent collisions involving very large energy transfers. The energy difference between the peak positions of the energy-shifted peak (E_M) and the unshifted peak (E_0) gives the most probable energy loss ($\Delta E_M = E_0 - E_M$), while the difference between the positions of the centroid of the shifted peak (E_A) and the unshifted peak gives the average energy loss ($\Delta E_A = E_0 - E_A$). The quantities $W = (E_2 - E_1)/E_M$ and $S = (E_2 - E_M)/(E_M - E_1)$ represent the width and the skewness of the energy distribution, respectively. E_1 and E_2 are the energy values at which the intensity in the energy-loss peak has half its maximum value. A typical electron-energy spectrum is shown in Fig. 2. The observed spectra were least-square fitted to a fifth-degree polynomial through an iterative type computer program to obtain the position of the energy-shifted and unshifted peaks. The statistical errors in the determinations of the peak positions of the energy-unshifted and energy-shifted peaks were estimated to be ±0.05 and ±0.3 channels, respectively, i.e., the net error in the energy-loss measurement was around ±0.4 keV (= ±0.35 channels). The *K* and *L* conversion electron peaks corresponding to the 662-keV γ ray in ^{137}Cs were used for energy calibration of the analyzer which was ~1.3 keV/channel.

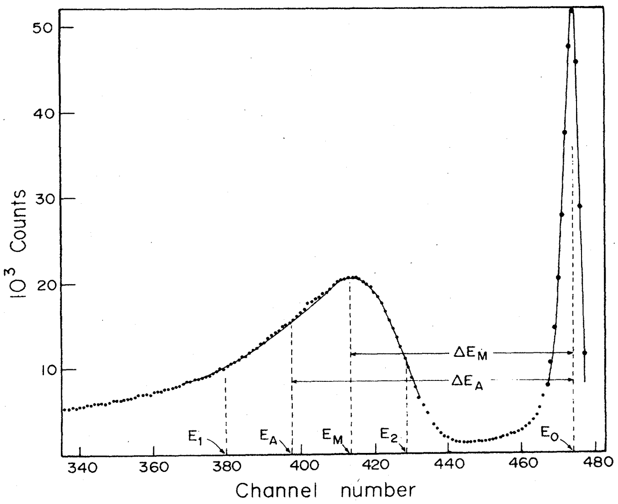

FIG. 2. Typical electron-energy-loss spectrum at a particular temperature. The solid line represents the least-squares-fit polynomial curve through the data points.

IV. RESULTS

It was found that the most probable energy loss generally showed a somewhat larger increase at T_C than the average energy loss. This seems to imply that the relatively infrequent close collisions resulting in large energy changes (which affect the value of ΔE_A but not that of ΔE_M) play a relatively insignificant role in the energy-loss anomaly. Henceforth, all references to the energy loss would signify only the most probable energy loss, that is, $\Delta E_M = \Delta E$. At this point it is proper to define the energy-loss anomaly as the difference $\Delta E(T_C) - \Delta E(T_R)$ where $\Delta E(T_C)$ and $\Delta E(T_R)$ are the energy loss at the Curie temperature T_C and at room temperature, respectively. The dependence of anomaly in ΔE on a number of parameters has been obtained from the present measurements and is given below.

A. Correlation with the magnitude of the dielectric anomaly

The electron energy loss as a function of temperature was measured with several crystals of TGS and BT with different values of $\epsilon = \epsilon(T_C)/\epsilon(T_R)$, where $\epsilon(T_C)$ and $\epsilon(T_R)$ are the low-frequency dielectric constant at temperature T_C and at room temperature, respectively. The dielectric constant of a given sample would depend upon the quality of the crystal and also on its thickness. However, in the present case, the dielectric anomaly is found to be largest for the thinnest crystal which is in contradiction to the trend observed for TGS.[4] Hence, in the present case the variation of the dielectric anomaly may be ascribed to the quality of the crystals, i.e., to impurities, imperfections, differences in domain sizes and patterns, and differences in the stress distribution due to the clamping of the crystals by electrodes. Observations on three different crystals of TGS (Table I) all cut normal to the b axis show that the crystal with the largest value of ϵ has the largest energy-loss anomaly ($\simeq 12\%$) and the crystals with smaller values of ϵ show correspondingly smaller values of the energy-loss anomaly (Fig. 3).

B. Dependence on the direction of the axes relative to beam direction

The energy loss in TGS was measured for the b-plate crystals with ferroelectric axis along the beam direction and for the c-plate crystal with ferroelectric axis normal to the beam direction. Figure 3 shows that the observed anomaly in the energy loss is larger when beam direction is along the b axis compared to the latter case where it is normal to the b axis. The effect is small but not totally absent in a c-plate crystal, presumably, because a small fraction of domains are still expected to be aligned along the beam direction. In addition, the divergence of the electron beam will also contribute to this effect.

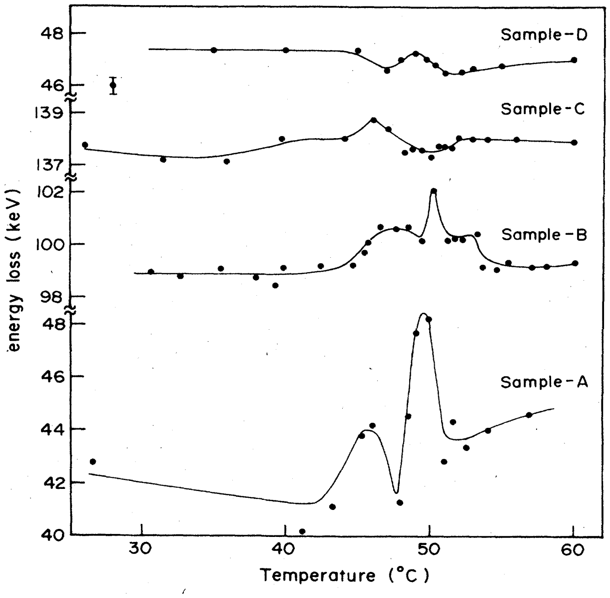

FIG. 3. Dependence of energy-loss anomaly on the magnitude of the dielectric peak and the direction of propagation of electrons in different triglycine sulfate crystals (see also Table I). The solid lines in Figs. 3 and 4 are for visual guidance.

C. Effect of an external dc field

The application of a dc voltage along the ferroelectric axis aligns a substantial fraction of domains in that direction. The coercive field in TGS is known[5] to be about 400 V/cm at room temperature. Energy-loss measurements in the TGS b-plate crystal showing the smallest dielectric and energy-loss anomalies (sample C) were repeated in the

TABLE I. Characteristics of the selected ferroelectric targets.

Sample label	Nature of sample	Thickness (mm)	T_C (°C)	$\frac{\epsilon(T_C)}{\epsilon(T_R)}$
A	TGS b-plate crystal	0.20	49.0	180
B	TGS b-plate crystal	0.40	49.0	22
C	TGS b-plate crystal	0.56	50.0	2.95
D	TGS c-plate crystal	0.21	49.8	1.18
E	BT polycrystalline	0.20	106	5.5
F	BT c-plate crystal	0.10	116	~30
G	BT c-plate crystal	0.20	121	~20

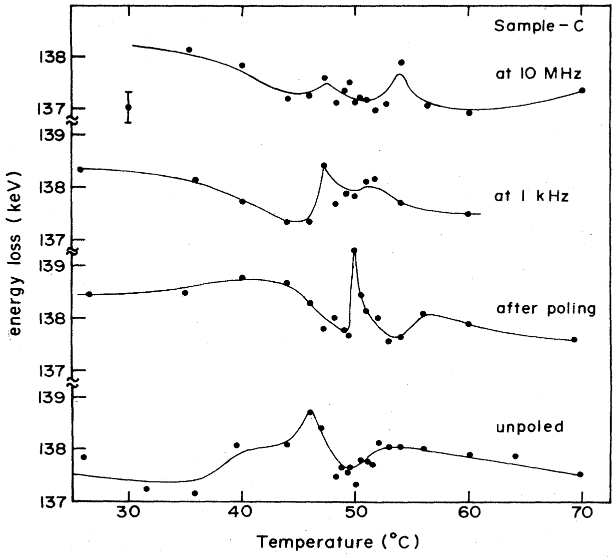

FIG. 4. Effect of applying steady (poling) voltages and small high-frequency voltages on a triglycine sulfate crystal.

presence of a steady electric field of about 500 V/cm applied across the electrodes. This resulted in definite changes in the ΔE versus T curve. The curve shows a peak at 46 °C with a large width in the absence of the external field, whereas the capacitance anomaly (measured *in situ*) was found at 50.0 °C. In the presence of the field, this peak increased in magnitude, decreased in width and appeared at exactly 50.0 °C (Fig. 4).

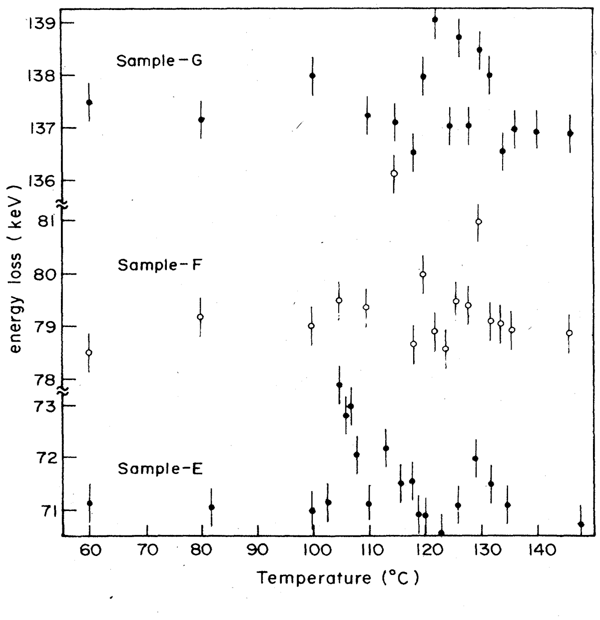

FIG. 5. Energy loss in polycrystalline and single crystal barium titanate samples (see also Table I).

D. Effect of an alternating electric field

Measurements were repeated with the TGS crystal (sample C) at 80 V/cm, peak-to-peak sinusoidal voltage at a frequency of 1 kHz and 10 MHz. Figure 4 shows a decrease in the anomaly in ΔE around T_C at 1 kHz which almost disappears at 10 MHz.

E. Effect in polycrystalline samples

Measurements of ΔE performed with a polycrystalline BT pellet (sample E) showed an energy-loss anomaly at 106 °C (see Fig. 5). The dielectric anomaly was also found at 106 °C in this sample. This large difference in T_C from the published value of 130 °C is possibly due to the impurities in the industrial grade BT sample. This confirms the view that the dielectric and energy-loss anomalies are correlated.

F. Structure of the energy-loss curve near the Curie temperature

In addition to the primary peak in the ΔE versus T curve, usually one or two subsidiary peaks were also observed near T_C. Since the scatter of the points in the baseline (far away from T_C) of the ΔE versus T curves is consistently within the error bars (± 0.4 keV), these additional features may be considered genuine. The secondary peaks were consistently observed above T_C for all BT samples (Fig. 5). On the other hand, both of the TGS samples (A and B) showed a broad peak on either side of the primary one. In sample C, these peaks become prominent only at high frequencies. However, the position and the intensity of the secondary peaks appear to be sample dependent.

G. Other changes near the Curie temperature

The skewness (S) of the energy-shifted curve plotted against T exhibited a 2–3 % dip near T_C in most samples. This indicated that the energy-loss peak became more symmetric near T_C. This effect was most prominent in sample A, which showed the largest dielectric and energy-loss anomalies. However, the FWHM (W) for the energy-loss peak shows no appreciable change with temperature. The general nature of the anomaly in ΔE was found to be independent of whether measurements were made in temperature increasing or decreasing mode. Contrary to the findings of Ref. 1, no appreciable difference in the mean values of ΔE between the paraelectric and ferroelectric phases was observed.

V. DISCUSSION

We shall now discuss the results presented in the preceding section and look for a plausible physical mechanism which can lead to the anomaly observed in the energy loss of electrons near T_C in ferroelectric substances. Our measurements indicate that a strong correlation exists between the observed energy-loss anomaly and the anomaly in the static dielectric constant. It is interesting to observe that the energy-loss anomaly is present even in polycrystalline samples. Such an observation rules out any effect of "channeling" of electrons on the temperature dependence of the energy loss. The inelastic scattering of electrons from domain walls or grain boundaries cannot contribute to the anomaly observed in our experiment since measurements were made in the transmission geometry.

The "density effect" proposed by Sternheimer[6] leads to an appreciable energy loss (EL) only for relativistic particles. The density effect-corrected expression for the EL per unit distance[7] involves the frequency-dependent dielectric function $\epsilon(\omega)$ of the medium. But this would not lead to a critical temperature dependence for the EL, mainly because the range of frequencies relevant to our problem is too high for $\epsilon(\omega)$ to show a critical anomaly. Similarly, the possible contribution of the "low-energy density effect" on the EL anomaly has been discussed and ruled out by Lagare and Umakantha.[1]

We will now consider the possibility of relativistic electrons producing local changes in the spontaneous polarization within the ferroelectric medium. The electric field produced by an electron at a distance d from its rectilinear trajectory is essentially transverse, since the longitudinal component has a vanishing time average. For simplicity, we consider a crystal cut normal to the ferroelectric axis in which cylindrical domains (typically having a diameter of 10^{-4} to 10^{-5} cm) extend from one face of the crystal to the other. In such a case, we may expect an electron to travel within a single domain. The electric field produced by the passage of a 624-keV electron is given by the usual relativistic formula,[8] and the peak transverse field varies from 30 MV/cm at a distance of 10 Å to 0.3 MV/cm at a distance of 100 Å from the path of the electron. If this field is larger than the coercive field in the medium and if the electron is traveling along the ferroelectric axis, any of the following situations may arise: (a) switching of dipoles and nucleation of 90° domains, (b) complete polarization reversal (180° domains), or (c) small damped oscillations of polarization about the ferroelectric axis. The processes (a) and (b) may occur only if the domain switching time $t_s(d)$ is smaller than the time interval $\Delta t(d)$, during which the field at a distance d from the electron path is larger than the coercive field. An accurate estimation of $\Delta t(d)$ is difficult because the coercive field is not strictly a material constant[9] but depends on various parameters, such as, the rise rate of the applied field, the time for which it is applied, the temperature, etc.

The domain switching time (t_s) for moderately high fields (up to a few kV/cm) can be related[10] to the domain-wall mobility (μ) through the relation

$$t_s = d\mu^{-1}E^{-1} , \tag{1}$$

where E is the switching field and d is the sample thickness. Between 10 kV/cm and 0.5 MV/cm the mechanism of switching has been found[11] to be similar to that at lower fields, but the exponent of E is ~ -1.4 rather than -1. In the absence of data at higher fields we assume relation (1) to be valid for the entire range of E. The reciprocal mobility β $(=\mu^{-1})$ has been found to depend linearly on T(°C) and in the case of $BaTiO_3$ the relation[12] is $\beta=\beta_0(1-T/T_C)$, where $\beta_0 \simeq 0.48$ for $0<T<T_C$.

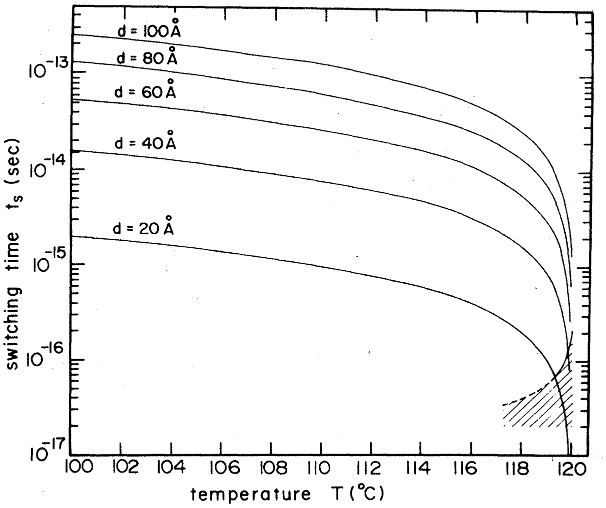

FIG. 6. Temperature dependence of the domain switching time t_s. T_C has been assumed to be 120 °C. The hatched area represents the domain switching zone.

Hence t_s decreases to zero as $T \rightarrow T_C$ following the relation:

$$t_s = 0.48\frac{d}{E}\left[1-\frac{T}{T_C}\right] . \tag{2}$$

Figure 6 shows the variation of t_s with T for different values of d. In order to obtain a rough estimate of the temperature range over which switching may occur, we consider $\Delta t(d)$ to be the time interval during which E falls to $0.001E_{\max}$. The corresponding "switching zone" is indicated in Fig. 6 by the hatched area. It is apparent from the figure that domain switching may take place *only* in the narrow temperature range just below T_C ($T-T_C \leq 0.1$ °C) provided $d \simeq 50$ Å or less.

The domain-wall energy in BT has been found[13] to be ~ 2 ergs cm^{-2} for 90° walls and ~ 10 ergs cm^{-2} for 180° walls. Our simple calculations have shown that it is possible for 90° domains to be nucleated up to a distance of 50 Å from the path of the electron, all along its length ($\sim 10^{-2}$ cm) when T is close to T_C. The total energy required to nucleate domains over this volume turns out to be ~ 10 keV, which has to be suppled by the electron. An important question that arises is whether domain switching is at all possible within such small time intervals as 10^{-16} to 10^{-17} sec. It has been suggested[14] that at very high fields, all the unit cells of the crystal (within the switching zone) would reverse polarization simultaneously, so that for infinitely large fields the crystal would switch infinitely fast. However, due to the extremely short duration of the field, or due to the specific crystal symmetry (e.g., in TGS), stable 90° domains may not form. In such a situation the domains would tend to rearrange or switch back, giving rise to damped oscillations of the polarization near T_C.

It follows from the above argument that the EL is not expected to increase at T_C when the electrons travel along a nonferroelectric axis because most of the domains would already be aligned transverse to the propagation direction.

The comparatively larger values of peak dielectric constant in some crystals could arise from the presence of a larger number of easily orientable, small-sized domains. Such a condition would also facilitate domain switching by the moving electrons and lead to a larger EL at T_C. On applying a dc field the total volume of domains polarized along the ferroelectric (and propagation) direction would increase, leading to a larger critical EL. The effect of applying 1 kHz and 10 MHz fields on the anomaly in TGS is interesting particularly because dielectric dispersion effects have been observed in this material[15] at much higher frequencies, such as, 10 GHz. Even at 10 MHz the domain pattern remains static as far as the fast electron is concerned. However, at any instant of time, the net component of polarization along the propagation direction is smaller, which may lead to a decreased EL anomaly at these frequencies.

VI. CONCLUSIONS

Our experiments have shown that the critical enhancement of the energy loss of fast electrons in different types of ferroelectric media is correlated to the magnitude and temperature of occurrence of the dielectric response anomaly. The effects of applying dc and high-frequency electric fields have been studied. Different physical mechanisms have been discussed among which domain nucleation and polarization oscillation appear to offer plausible explanation of the general features of the observed phenomena. An exact calculation of the magnitude of the critical energy dissipation is expected to be difficult since a molecular-level treatment of domain switching and growth mechanisms is quite complicated. Also, the occurrence and frequency dependence of the subsidiary peaks in the ΔE versus T curve cannot be accounted for satisfactorily at this stage. Further investigations in this area may lead to new light on dynamic critical effects in ferroelectrics.

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