Anomalous Energy Loss of Electrons in Ferroelectrics at the Curie Temperature

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Experimentally it is found that the energy loss of 620- and 942-keV electrons in barium titanate, as well as that of 942-keV electrons in triglycine sulphate, is anomalously high at the Curie temperature. The energy loss is also noticeably smaller in the ferroelectric state than in the paraelectric state.

It is well established that the energy loss of high-energy charged particles in a condensed medium is affected by the electronic polarizability of the atoms of the medium, leading to the density effect.[1-5] There is also a much smaller effect, the low-energy density effect, due to the changes in the oscillator strengths of the outer electrons of the atoms depending on the state of the condensed medium.[6] These effects do not predict any anomalous increase in the stopping power of a medium when the phase of the medium changes, nor has any such increase been reported in the literature so far. In particular, no theory of density effect has been developed with reference to a ferroelectric medium. In this paper we report our experimental results which show that barium titanate (BT) and triglycine sulphate (TGS) exhibit anomalously high stopping power at their ferroelectric Curie temperatures.

We specially selected BT and TGS as targets because, apart from possessing convenient Curie temperatures, they are representative of two types of ferroelectrics. The unit cell of BT has an electric dipole moment in the ferroelectric state only and not in the paraelectric state, the ferroelectric-paraelectric transition being displacive type. On the other hand, the unit cell of TGS has an electric dipole moment in both the states, the transition being order-disorder type.[7] Thus a comparison of their stopping powers should bring out the role of electric dipole moment of the unit cell in energy loss of electrons.

In a fixed-geometry experiment the spectrum of internal-conversion electrons (from a source) transmitted through a thin ferroelectric target was measured as a function of target temperature. The assembly, consisting of the source, the target, and the detector, was placed in a vacuum chamber. The diameters of the source, the target, and the detector were 1, 0.8, and 1 cm, respectively; the target was 5 cm from both the source and the detector. The electron spec-

trometer consisted of a selection-grade NE Si(Li) detector, NE-4660 bias power supply, NE-5289 charge sensitive preamplifier, ND-520 linear amplifier, and ND-1100 multichannel analyzer. The detector was maintained to 10 °C by immersion in an ice-water mixture of the free end of a cold finger attached to the detector.

The spectrometer was first calibrated with a set of internal-conversion electron sources. The long-term stability of the system was checked by repeated observation of the full width at half maximum (FWHM) of the 624-keV internal-conversion peak of ^{137}Cs and by calculating the most probable energy by fitting a Gaussian to the top (above 60%) of the peak. It was found that the FWHM retained a value of 8 keV and the least-squares-fitted energy of the peak remained constant within ± 0.5 keV. Similarly, the uniformity of thickness of a few polycrystalline targets of BT and a few single-crystal targets of TGS was checked by observing the FWHM of the transmitted 624-keV peak of ^{137}Cs and the targets with minimum value of FWHM were selected for measurement of energy loss.

The selected target was placed between two thick aluminum plates with a circular opening at the center allowing the incident electrons to pass through the target. The target was heated indirectly by heating the aluminum plates electrically. Two 2.5-mg/cm^2 aluminum foils were placed across the faces of the aluminum plates to achieve better uniformity of temperature across the faces of the target. An aluminized Mylar sheet placed in front of the detector shielded it from both light and heat. The target was first taken through three temperature cycles of slow heating and cooling. The temperature of the target was controlled by a temperature control unit and the temperatures of the target, detector, and ice-water mixture were continuously monitored. They were steady within ± 0.25 °C. The spectral measurements were made only 60 min

after the target temperature stabilized.

The ^{137}Cs source was prepared in our laboratory and the effective energy of the internal-conversion line was 620 keV after correction for the window thickness. The ^{207}Bi source, supplied by New England Nuclear, was fabricated for use in vacuum and had a 18.8-mg/cm^2-thick Be window. Thus the effective energy of the incident electrons was 942 keV. After the calibration of the spectrometer, the spectrum of an internal-conversion line was recorded and by fitting of a Gaussian to the top (above 50%) of the peak, the least-squares-fitted channel number was determined. This channel number was taken to correspond to the effective energy of the internal conversion line. Similarly the spectrum of electrons transmitted through the target at each temperature was recorded and the most probable energy of the transmitted peak was found by least-squares-fitting a Gaussian to the top of the peak. The difference between these two energy values is taken, after correction for the small energy loss in the two aluminum foils covering the target, as the most probable energy loss ΔE.

While the spectrum was being recorded with the BT target, the stability of the spectrometer was checked by feeding to the test input of the NE-5289 preamplifier pulses from a precision pulser; in the case of the TGS target, a small part of the crystal was deliberately cut to transmit some incident electrons without any attenuation and this peak provided an internal check for the stability of the system. Repeated recordings of the spectra showed that the error in ΔE was ± 0.5 keV; the statistical error due to the finite number of counts accumulated in the channels was less than this. Systematic error in ΔE may be larger than ± 0.5 keV but this error is the same at all temperatures of the target. Thus the variations in ΔE are more accurate than the ΔE values themselves.

After each set of measurements, the target was cooled to room temperature and ΔE was measured again; it was found to agree with the original value at room temperature within experimental error. After this the target was examined under a magnifying lens and found not to have undergone any mechanical deformation.

The experimentally determined most probable energy loss ΔE, measured as a function of target temperature, is shown in Fig. 1(a) for 620-keV electrons in a polycrystalline BT target of 30 mg/cm^2, Fig. 1(b) for 942-keV electrons in a polycrystalline BT target of 50 mg/cm^2, and Fig. 1(c)
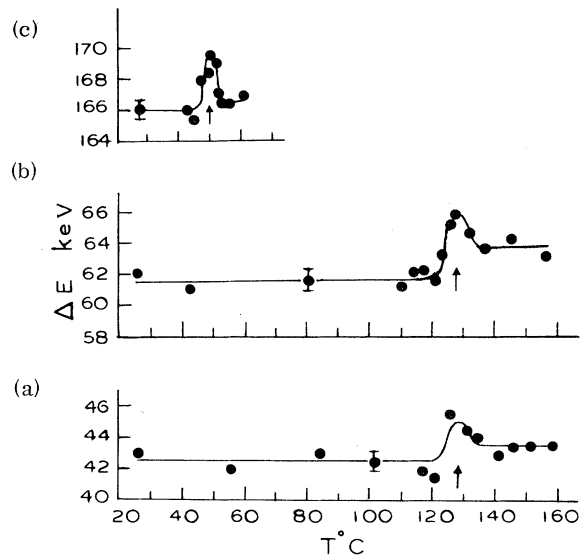

FIG. 1. Most probable energy loss, E, of electrons of (a) 620 keV in a 30-mg/cm^2-thick polycrystalline barium titanate target, (b) 942 keV in a 50-mg/cm^2-thick polycrystalline barium titanate target, and (c) 942 keV in a 95-mg/cm^2-thick single-crystal triglycine sulphate target measured as a function of target temperatures T°C. The solid lines are smooth curves through the experimental points. The arrows indicate the Curie temperatures.

for 942-keV electrons in a single-crystal target of TGS of 95 mg/cm^2. Typical experimental error is ± 0.5 keV and is shown at one point in each case.

In the case of BT we see from Fig. 1(a) that ΔE remains constant at 42.5 keV, within experimental error, over the ferroelectric state of the target, increases to a maximum of 45.0 keV at the Curie temperature of 127 °C, and assumes a higher constant value at 43.5 keV over the paraelectric state; the corresponding values for Fig. 1(b) are 61.5, 65.5, and 63.5 keV. We see from Fig. 1(c) that in the case of TGS, ΔE has, within experimental error, the same value of 166 keV over both the ferroelectric and paraelectric states, though the values over the paraelectric state are consistently higher; at the Curie temperature of 50 °C, ΔE increases to a maximum value of 169.5 keV.

The important feature of our results is that the most probable energy loss exhibits an anomalously high value by about 2%–3% in the immediate neighborhood of the Curie temperature in all the three cases. This cannot be attributed to any of the known effects. In the first place, the change in the areal density of BT is less than 0.01% at

the Curie temperature[8] and so the correction to the observed ΔE for the thermal expansion of the target is negligible; this is so for TGS also. Secondly, Sternheimer estimates that the low-energy density effect, which takes into account the changes in the mean excitation potentials of the atoms in the paraelectric and ferroelectric states, leads to less than 1% change in the stopping power in the two states for 2-MeV electrons.[9] For the 620- and 942-keV electrons used in our experiment this effect would be much less. In our experiment the angular divergence of the beam incident on the target was about 12° and that of the transmitted beam reaching the detector was also about 12°. Apart from the angular divergences being so large, the anomalous increase has been observed even for a polycrystalline target of 50 mg/cm² (90 μm). Thus channeling is not likely to be responsible either. We may conclude that the observed anomalous increase in ΔE at the Curie temperature is a new effect unpredicted by any of the existing theories, and also that this new effect increases the stopping power of the medium unlike the density effect.

As this anomalous increase is present only in the neighborhood of the ferroelectric Curie temperature, we may recognize it as a critical phenomenon involving the electric dipole moments in the medium. Since TGS, whose unit cells have the same electric dipole moments in both the states, also exhibits this effect, this effect does not merely depend on the individual dipole moments of the unit cells but depends on the short-range order that exists between these dipole moments in the neighborhood of the Curie temperature. Or, in other words, in the neighborhood of the Curie temperature an incident electron interacts with a cluster of unit cells and loses its energy to the cluster by inducing greater disorder in the dipole moments in the cluster.

We may also note that in the case of TGS, whose unit cells have the same electric dipole moment in the ferroelectric and paraelectric states, the observed values of ΔE in the two states are almost the same for 942-keV electrons. On the other hand, in the case of BT,

whose unit cells have an electric dipole moment only in the ferroelectric state, the observed value of ΔE is about 3% less in the ferroelectric state compared to that in the paraelectric state for 942-keV electrons; such a feature is seen for 620-keV electrons also. Since the areal density of BT decreases by less than 0.2% when the target temperature increases from 40 to 140 °C, the effect of thermal expansion on ΔE is negligible. Though a part of the decrease in ΔE in the ferroelectric state of BT can be attributed to the low-energy density effect, a major part may be attributed to the role played by the electric dipole moment of the unit cell.

In conclusion we may state that our experimental observations establish for the first time that the electric dipole moments of the unit cells of a ferroelectric medium also play a role in energy loss of high-energy charged particles passing through it. Precise measurements of energy loss at the Curie temperature may offer a method of investigating the dynamics of short-range order in a ferroelectric at the Curie temperature. More precise measurements of the energy loss, especially at higher electron energies, and also theoretical investigations of this new mode of energy loss in ferroelectrics are necessary.

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[1]E. Fermi, Phys. Rev. 57, 485 (1970).

[2]O. Halpern and H. Hall, Phys. Rev. 73, 477 (1948).

[3]R. M. Sternheimer, Phys. Rev. 88, 851 (1952), and Phys. Rev. B 3, 3681 (1971).

[4]A. Bohr, Dan. Vidensk. Selsk. Mat. Fys. Medd. 24, 19 (1948).

[5]A. Crispin and G. M. Fowler, Rev. Mod. Phys. 42, 290 (1970).

[6]R. M. Sternheimer, Phys. Rev. 93, 351 (1954).

[7]F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, New York, 1962).

[8]T. Mitsui, *Ferroelectric and Antiferroelectric Substances*, Landolt-Börnstein: Numerical Data and Fundamental Relationships in Science and Technology, Group 3, Vol. 3, edited by K. H. Hellwege and A. M. Hellwege (Springer-Verlag, New York, 1976).

[9]R. M. Sternheimer, private communication.