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Mössbauer Effect in Ferroelectric $BaTiO_3$†

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The Mössbauer effect for Fe^{57m} in the $BaTiO_3$ lattice has been studied from 300 to 1200°K with particular emphasis on the region near the Curie temperature. The Mössbauer probe seems to serve as a useful tool for the study of ferroelectrics. The electric-field gradient as seen by the probe at room temperature is -0.52×10^{14} esu cm^{-3} and is closely proportional to P_s^2 as the spontaneous polarization P_s varies with temperature. The strength of the resonant absorption was also determined as a function of temperature in the region above T_c. Much above T_c these measurements are compatible with a Debye temperature of 450°K. However, as the Curie temperature is approached, the Lamb-Mössbauer factor decreases appreciably. These results are discussed in the light of Cochran's theory of ferroelectricity. From the isomer shift at room temperature (0.50 ± 0.02 mm/sec with respect to 310 stainless steel) the over-all degree of ionicity is estimated to be $60\pm20\%$. The temperature shift shows a discontinuity at T_c and is attributed to the change in covalent binding.

I. INTRODUCTION

It has long been recognized that ferroelectricity in the ABO_3-type compounds, of which $BaTiO_3$ is a typical member, is closely associated with (1) intense electric field at the B lattice site, (2) temperature-dependent homogeneous transverse-optical B-O-B mode, (3) nature of the B-O bond, and (4) displacement of the B ion in the surrounding oxygen octahedron.[1] In view of the important role played by the B ion, several attempts have been made to investigate its environment.

The nuclear-quadrupole-resonance studies[2] of Nb^{93} in $KNbO_3$ have shown that the Nb ion is subjected to a strong electric-field gradient (EFG). Unfortunately, the quadrupole resonance of Ti in $BaTiO_3$ is not possible because of the low abundance of Ti^{47} and Ti^{49} and their small magnetic moments. However, x-ray K absorption and emission spectra of Ti in $BaTiO_3$ has shown that the Ti bond is partially ionic.[3] Hornig and co-workers[4] have studied the electron paramagnetic resonance of substituted Fe^{3+} occupying the Ti^{4+} site in $BaTiO_3$. Similar studies have recently been reported for Fe^{3+} in $SrTiO_3$ [5] and $PbTiO_3$ [6] which have indicated the existence of strong axial field.

With the discovery of the Mössbauer effect (ME), investigations of exceedingly small perturbations in the nuclear levels caused by the solid-state properties of the lattice have been made possible. Indeed, numerous investigations have already been reported on ferromagnetic interactions using the (ME).[7] However, no attempt has yet been made to study the effect of a ferroelectric lattice in which the electric dipoles are aligned along one of the easy directions, for example, pseudocubic $\langle100\rangle$ in tetragonal $BaTiO_3$. Such a study is also interesting from the point of view of lattice dynamics since Cochran[8] and Anderson[9] have shown that one of the homogeneous (wave vector $\mathbf{k}=0$) transverse-optical modes progressively decreases in frequency as the Curie temperature (T_c) is approached from the higher temperature side. This temperature dependence is expected to manifest itself in the variation of the Lamb-Mössbauer factor in the vicinity of T_c.

This paper reports the temperature variation of (1) EFG caused by the lattice at the titanium site as seen by the iron probe, (2) the area under the resonance curve and hence the strength of the resonant absorption, and (3) the center shift. The EFG follows closely the variation of the square of spontaneous polarization P_s^2 with temperature and disappears at T_c. From the isomeric shift it is possible to estimate the over-all degree of ionic character, which is roughly $60\pm20\%$. The area under the resonance curve has an anomalous variation in the vicinity of T_c. The significance of these observations in the theory of ferroelectricity is discussed.

II. EXPERIMENTAL

A. Preparation of Source and Absorber

For (ME) studies it would be advantageous to use Fe^{57}-doped $BaTiO_3$ absorbers with a metallic host-lattice source, as this would not give rise to possible

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† Work supported by the National Bureau of Standards, Washington, D. C.

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[3] M. A. Blokhim, Doklady Akad. Nauk SSSR **95**, 965, 1165 (1954). E. E. Vainshtein *et al.*, Izv. Akad. Nauk SSSR, Ser. Fiz. **20**, 984 (1956); Doklady Akad. Nauk SSSR **114**, 53 (1957) [English transl.: Soviet Phys.—Doklady **2**, 207 (1957)]; **117**, 597 (1957) [English transl.: Soviet Phys.—Doklady **2**, 518 (1957)].

[4] A. W. Hornig, R. C. Rempel, and H. E. Weaver, J. Phys. Chem. Solids **10**, 1 (1959).

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[6] D. J. A. Gainon, Phys. Rev. **134**, A1300 (1964).

[7] The most recent publication on the Mössbauer effect is by G. K. Wertheim, *Mössbauer Effect: Principles and Applications* (Academic Press Inc., New York, 1964).

[8] W. Cochran, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1960), Vol. 9, p. 387.

[9] P. Anderson, in *Fizika Dielektrikov*, edited by G. I. Skanavi (Akademica Nauk SSSR Fizicheskii Inst. im P. N. Lebedeva, Moscow, 1960).

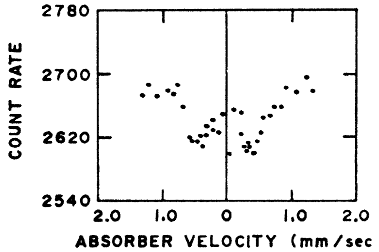

FIG. 1. Velocity spectrum of one-mole-percent Fe^{57}-doped absorber matched against Co^{57}-copper source. $\Delta E = 0.81 \pm 0.05$ mm/sec, $\delta = 0.45 \pm 0.04$ mm/sec.

complications of the aftereffects of K capture of Co^{57}.[10] In order to perform such an experiment effectively, the Fe^{57} absorber nuclei should have an areal density of about 0.1 mg cm^{-2} for adequate absorption. It is necessary to be judicious while doping a solid, for it has been shown that on doping $BaTiO_3$ with iron the tetragonality of the lattice decreases almost linearly with impurity concentration and disappears at about 5-mole percent.[11] This is associated with a lowering of T_c and weakening of the ferroelectric action. It is therefore advisable not to use high concentrations of iron because then we would be destroying the effect we intend to measure. If one reduces the concentration the absorber has to be thicker and thus one weakens the primary 14.4-keV beam and enhances the Compton-degraded background caused by the higher energy radiation from Co^{57}. Figure 1 shows the velocity spectrum obtained using a Co^{57}-copper source and $BaTiO_3$ doped with one mole percent iron as an absorber. The absorption is barely 3% and hence its variation with temperature cannot be studied.[12] Because of these factors, the (ME) study of $BaTiO_3$ lattice as a host for absorber nuclei is highly limited and hence in the present investigation measurements have been made employing $BaTiO_3$ as a source lattice. Quite apart from the low absorption it will be shown in paper II that ΔE in an Fe^{57}-$BaTiO_3$ absorber does not represent the true EFG.

Large single-crystal plates (c plates) were grown following the Remeika technique. These crystals were etched in hot phosphoric acid to expose fresh surfaces. About 100-μCi activity as aqueous solution of $Co^{57}Cl_2$ was evaporated from the crystal surface. The active residue was thermally diffused for 1 h in a hydrogen-atmosphere furnace at 850°C. The reducing atmosphere produced a negligible amount of the coloration normally associated with oxygen vacancies. Rough measurements for estimating diffusion penetration using an etching technique yielded a mean diffusion depth of about 1 μ over a region of 5 mm diameter. Thus the concentration of cobalt impurity did not exceed 0.02 mole percent and was not expected to alter the ferroelectric characteristics.

Of the batch of six crystals with diffused activity, two were heated for 2 h at 1100°C in air and then thermally quenched. No particular care was taken to control the quench duration, but it was estimated that the crystals cooled to room temperature in about a minute. The work presented here offers evidence to suggest that the quenching treatment aids in creating a perfect-lattice local environment (absence of near-neighbor charge-compensating oxygen vacancies around the majority of the Mössbauer probes). The remaining four crystals were subjected to different treatments so as to produce different local environments. In these, several complications such as near-neighbor vacancy, multiple ionized states, etc. arise and will be discussed in another paper. In this paper we restrict ourselves to the discussion of (ME) in a $BaTiO_3$ host lattice when a Fe^{57m} probe "sees" a nearly perfect-lattice local environment in the trivalent charge state.

B. Location and Charge State of the Mössbauer Probe

Extensive evidence exists which leads to a positive inference of the location and charge state of the cobalt and iron impurities in $BaTiO_3$. Hurd *et al.*[13] from their studies on the magnetic susceptibility of cobalt-doped $BaTiO_3$ have shown that Co enters the lattice substitutionally as a divalent ion replacing Ti^{4+}. Size considerations (Co^{2+}, 0.77 Å; Ti^{4+}, 0.64 Å; Ba^{2+}, 1.38 Å) also favor Ti replacement. The recent results of Kudzins[14] on the dielectric properties and optical absorption establish such a substitution conclusively. It is extremely unlikely that the recoil associated with the electron-capture process is sufficiently energetic to displace the daughter Fe^{57m} from the substitutional site. Moreover, iron impurities are also known to occupy Ti sites as Fe^{3+} in the perovskites $BaTiO_3$,[4] $SrTiO_3$,[5] and $PbTiO_3$.[6] Criteria for impurity substitution in the perovskites have been discussed by Müller.[15]

It remains now to discuss the charge state of Fe^{57m} prior to 14.4-keV gamma emission. Although the trivalent state is normally preferred, it is of interest to examine the aftereffects of electron capture on the daughter Fe^{57m}. Divalent Fe^{57m} produced on electron capture (83.5% K capture; 16.5% L capture) by the $(Co^{57})^{2+}$ has its nucleus in the second excited state and has a hole in the inner electronic shell (K or L shell). Atomic de-excitation by the emission of x rays and Auger electrons yielding higher charge states of Fe^{57m} will proceed simultaneously with nuclear de-excitation to the first excited isomer state by the emission of the 123-keV

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gamma photons. The first excited state has a mean life of $\tau \approx 10^{-7}$ sec. The highly ionized Fe^{57} ions may recapture free electrons in a time shorter compared with 10^{-7} sec and relax over to the stable state in the lattice. In metallic host lattices, the relaxation time of these highly ionized short-lived charged states is of the order of 10^{-12} sec, and almost all nuclei go over to the stable state prior to the emission of recoil-free radiation. However, in dielectric media the relaxation times may be of the order of 10^{-7} sec (as for[10] Fe^{57m} in CoO) and in such cases the Mössbauer probes will have different charge states. These will be reflected in the Mössbauer spectrum as two (or more) resonance dips because of the different isomer shifts for different charge states, or by the broadening of the absorption line due to time-varying electric fields at the nuclei. It may be noted that the relaxation time not only depends on the general properties of the lattice, but would also depend sensitively upon the local environment of the Mössbauer probes. Defects such as oxygen vacancies may alter the relaxation times considerably. Indeed, in samples heated in hydrogen atmosphere for long periods, facilitating a greater number of oxygen vacancies, the spectra reveal two distinct charge states. For samples heated to 1100°C in air and then quenched, only one charge state was indicated although the spectrum was a little broad.

C. Velocity Spectrometer

The Mössbauer data were collected in transmission using a 310-stainless-steel absorber to which linear velocity relative to the source was imparted by the conventional constant-velocity mechanical drive. The Mössbauer radiation was detected by a 40-mm diameter, 1-mm thick NaI:Tl scintillator coupled to a RCA 6810A photomultiplier. The scintillation spectrometer had a resolution of 40–45% for the 14.4-keV radiation, which was fed into separate scalers for positive and negative velocities and accumulated to 2.5×10^4 counts for each velocity setting. The total time of operation of each gate was recorded by time signals from a 1-kc/sec crystal-controlled oscillator. The source was taken to high temperatures in a furnace. The radiation was taken out of the furnace through a thin aluminum window. The source was pressed to a copper block where also a Pt-(PtRh) thermocouple was clamped. The source being small, good uniformity of temperature was obtained; the instability never exceeded 2°C.

The velocity spectrum below T_c was a composite of two closely spaced Lorentzians which were resolved in the manner suggested by Shirane *et al.*[16] Calculated curves to match those observed were obtained by superposing doublets each given by the formula

$$y=\frac{y_0}{1+0.75(2x/\Gamma)^2+0.25(2x/\Gamma)^4},$$

where y_0 is the depth of an individual dip, x is the distance from the middle of the dip, and Γ is the full width at half the maximum intensity. Above T_c the observations could be fitted to a single Lorentzian.

III. RESULTS

A. Electric Field Gradient and Isomer Shift

The Mössbauer spectra at various temperatures are shown in Fig. 2. The spectrum at room temperature shows two closely spaced dips centered at 0.28 and 0.74 mm/sec while the spectrum at a temperature such as 142°C shows a single dip centered at 0.42 mm/sec. It is necessary to decide, before we proceed with further discussion, whether the two dips at room temperature result from quadrupolar interaction or from two charge states of the Mössbauer probe. In ferroelectrics this question can be unambiguously answered by biasing

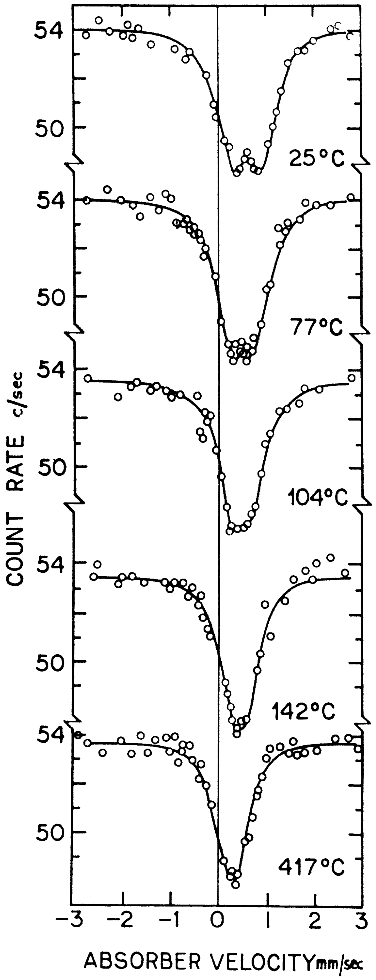

FIG. 2. Typical spectra for BaTiO$_3$ source-lattice at different temperatures. The absorber is one-mil 310 stainless steel (obtained through the courtesy of Dr. G. K. Wertheim, Bell Telephone Laboratories).

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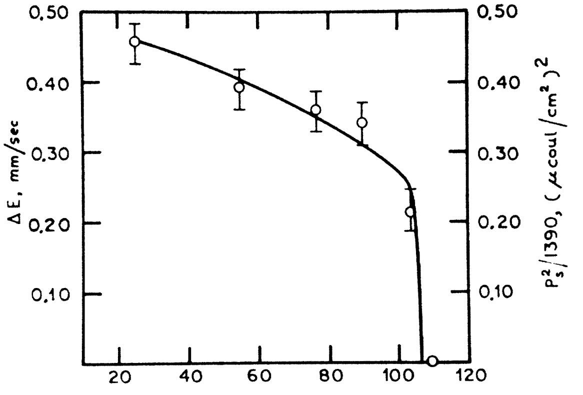

FIG. 3. Variation of the quadrupole splitting with temperature is represented by open circles. The solid line indicates, on a matching scale, the variation of the square of spontaneous polarization.

the crystal with an electric field. In tetragonal $BaTiO_3$ (5–120°C) the principal EFG axis is along the tetragonal c axis, and since ferroelectrics of the $BaTiO_3$ type exhibit both 180° and 90° domains, the principal axis may be in different directions in different domains and correspond with one of the ⟨100⟩ pseudocubic axes. In a multidomain crystal, as in the present case, the $\pm\frac{3}{2}\rightarrow\frac{1}{2}$ and $\pm\frac{1}{2}\rightarrow\frac{1}{2}$ transitions of the quadrupolar split spectrum would have intensity ratios depending upon the domain distribution. Fortunately, in ferroelectrics one can align the direction of the spontaneous polarization and thus the principal axis of the EFG, by the application of an electric field. On the application of a biasing field of 5 kV/cm along a direction perpendicular to the crystal plate, the intensity ratio was altered so that the dip nearer zero velocity became considerably more intense than the other dip. This confirms that the two dips observed at room temperature arise out of the quadrupolar splitting and further that the interaction is negative. Further confirmation was afforded by orientation experiments.

The precise location of the resonance dips was obtained by the method of curve fitting referred to above. It is found that on raising the temperature the two components of the split spectrum approach each other and finally at and above 107°C merge into a single resonance. The variation of ΔE, the quadrupole splitting, with temperature is shown in Fig. 3. The determination of T_c through the disappearance of ΔE agrees very well with the determination of T_c through the dielectric properties (dielectric constant and dielectric hysteresis), thus indicating that at least in $BaTiO_3$ the impurity probe serves well in the investigation of the environment of Ti ion.

The center of gravity of the split spectrum at room temperature corresponds to 0.50±0.02 mm/sec. From the systematics of isomer shift[17] it may be inferred that the charge state of the probe is trivalent. Besides, the disappearance of the EFG at T_c (at which the lattice becomes cubic) precludes the Fe^{2+} ion, which would have its own field gradient. Indeed, it is fortuitous that the Mössbauer probe is the ${}^6S_{5/2}$ Fe^{3+} ion and thus capable of measuring the crystalline EFG through the quadrupole interaction with $I=\frac{3}{2}$ of Fe^{57m}. The splitting ΔE is given by

$$\Delta E=\tfrac{1}{2}e^2(1-\gamma_\infty)qQ(1+\tfrac{1}{3}\eta^2)^{1/2},$$

where γ_∞ is the Sternheimer antishielding factor,[18] η the asymmetry parameter, q the crystalline EFG, and Q the quadrupole moment of Fe^{57m}. In tetragonal $BaTiO_3$, $\eta=0$. Using Sternheimer's recently determined value of $\gamma_\infty=-9.14$ and[19] the value of $Q=+0.18b$ arrived at by Watson and Freeman[20] after careful analysis of the available experimental data, one can determine the lattice EFG and compare it with the theoretically computed value from the knowledge of the monopole and dipole distribution around the probe. Figure 3 shows the variation of the experimentally determined EFG's with temperature. On the same figure is plotted the variation of P_s^2 with T. It is significant that EFG is closely proportional to P_s^2.

The EFG at the Fe nucleus occupying the Ti^{4+} site in the lattice is given by

$$\frac{\partial E_z}{\partial z}=(1-\gamma_\infty)\sum_i{}' \frac{\partial^2}{\partial z^2}\left(\frac{q_i}{r_i}+\frac{\boldsymbol{\mu}_i}{r_i^2}\right),$$

where q_i is the effective charge, $\boldsymbol{\mu}_i$ the dipole moment at the ith site in the lattice, and r_i the distance of the field point from the ith site. Figure 4 shows the structure of $BaTiO_3$ in the tetragonal phase and from the knowledge of δz_{OI}, δz_{OII}, and δz_{Ti} one can compute the r_i's. The values of the displacements were taken from the

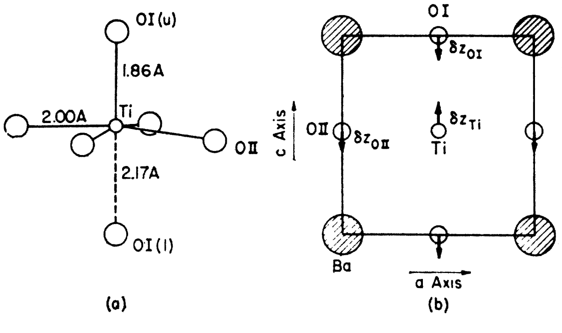

FIG. 4. Schematic diagram showing the relative displacements and the bond lengths of the $BaTiO_3$ ions. (Taken from Ref. 1, Fig. IV-33, p. 153.)

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neutron-diffraction measurements of Frazer *et al.*[21] The dipole moments were calculated from the knowledge of spontaneous polarization, following Slater.[22] It is seen that the EFG cannot be computed unless one knows the effective charges at various lattice sites. Various estimates have been made about the degree of covalency of the $BaTiO_3$ lattice. Kinase and Takahasi[23] and Triebwasser[24] estimate it at 50%. Fortunately, Mössbauer measurements give a clue to the degree of covalency through the isomer shift of the spectrum.

The isomer shift is given by

$$\delta=\tfrac{2}{5}\pi Ze^2[R_1^{2\rho}-R_0^{2\rho}][|\psi(0)|_A^2-|\psi(0)|_S^2],$$

where R_1 and R_0 are the effective charge radii of the isomeric and ground state of the nucleus, and $|\psi(0)|_A^2$ and $|\psi(0)|_S^2$ are the s-electron densities at the absorber and source nuclei, respectively. Referred to a standard absorber, the variation of δ would give the variation of $|\psi(0)|_S^2$ and through it some information about the electronic structure of the source atom. In simple salts such as aurous halides, the isomer shift varies linearly with ionicity of the lattice[25] as determined by Pauling's formulation.[26] However, in ferrous and ferric salts we have found that δ does not vary linearly with covalency because of the $3d$-$4s$ and s-p overlap.[25] However, the plot between isomer shift and ionicity of the bond for various ferric salts can serve as a useful calibration curve for the determination of the ionicity of a given salt. It may be emphasized that one merely gets an approximate idea of the ionicity, since the isomer shift cannot be measured accurately. Following this procedure we find that the ionicity of $BaTiO_3$ is 60±20%. This value is in close agreement with that inferred by Kinase and Takahasi[23] and by Triebwasser.[24]

Using 60% for the value of the ionicity, we have computed the field gradient due to the crystal lattice by the lattice-sum method, the summation extending over five unit cells on all sides of the field point. (See Table I.) It is interesting to observe that the EFG determined experimentally agrees fairly well with that computed as above.

Our results indicate the following: (1) The Mössbauer probe serves adequately in the investigation of the cooperative phenomenon between electric dipoles in ferroelectric $BaTiO_3$ and undergoes the displacement of the substituted Ti ion. (2) The EFG at room temperature is -0.52×10^{14} esu/cm³. (3) The EFG follows closely the variation of P_s^2 with temperature. (4) The over-all degree of ionicity is 60±20%.

TABLE I. Experimentally determined and computed EFG's (in 10^{14} esu cm^{-3}).

Experiment[a]	100% Ionic	60% Ionic
−0.52	−0.457	−0.513

[a] Obtained from the room-temperature quadrupole splitting using $Q=+0.18b$ and $\gamma_\infty=-9.14$.

B. Measurements of the Recoilless Fraction and Estimation of the Debye Temperature as Seen by the Probe

The strength of the resonant absorption can be obtained from the area A above the dips in the transmission curve normalized to unity for "*off resonance.*" For an isolated absorption dip, as above T_c, having a Lorentzian shape of width Γ, the area is given by $A=(\frac{1}{2})\pi nf_sf_a\sigma_0\Gamma G(nf_a\sigma_0)$, where f_s and f_a are the Lamb-Mössbauer factors for the source and absorber, σ_0 is the "*on-resonance*" value of the absorption cross-section for gamma radiation, and the function G is given in graphical form by Havens and Rainwater.[27] By running the absorber against a Co^{57}-copper source the characteristics of the absorber can be determined in terms of the known f factor for copper. Thus, above T_c, the factor f_s is proportional to the area under the resonance curve. f_s is given by

$$f_s=e^{-2W},\quad W=3(E_R/k\Theta_D)[\tfrac{1}{4}+(T/\Theta_D)^2\phi(T/\Theta_D)],$$

where $E_R=E_0^2/2Mc^2$ is the energy of free recoil of the nucleus of mass M, Θ_D is the Debye temperature, and ϕ is a tabulated integral.[28] Figure 5 shows the variation

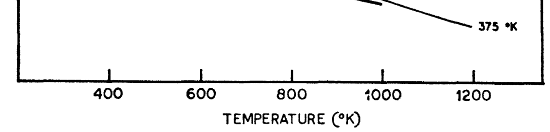

FIG. 5. Thin lines represent the expected variation of the resonant fraction for five different Debye temperatures. Thicker lines represent the resonant fractions computed from the experimentally determined areas above the Mössbauer dips and assuming the validity of each of the five temperatures.

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[28] M. W. Holm, *Atomic Energy Commission Research & Development Report IDO-16399*, 1957 (unpublished); A. H. Compton and S. K. Allison, *X-rays in Theory and Experiment* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1935), p. 437.

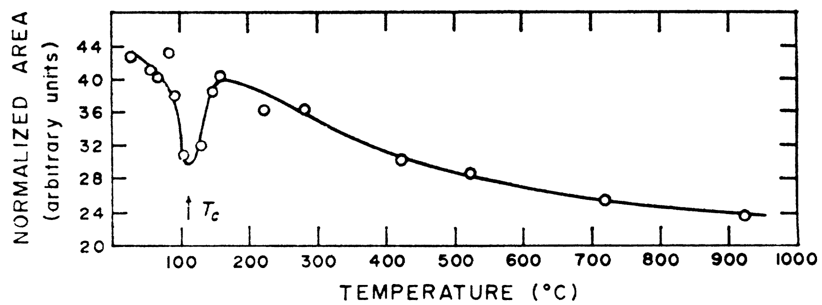

FIG. 6. Temperature variation of the normalized area of Fe^{57m}-$BaTiO_3$ source spectrum showing the marked anomaly in the vicinity of the Curie temperature T_c.

of the resonant fraction determined from the area by the choice of the constant of proportionality, against the variation of f_s with T for various Θ_D's. It is seen that above T_c they are compatible with a Debye temperature of 450°K. Figure 6 shows the actual area versus T. It is interesting to point out, however, that as one approaches T_c the area under the resonance curve decreases rather sharply, reaches a minimum at T_c, and again rises below T_c. The reduction in the strength of the resonance curve in the vicinity of T_c is very striking and suggestive in view of Cochran's theory of ferroelectricity. No estimate of the Debye temperature could be made below T_c because the temperature range available is very limited ($BaTiO_3$ undergoes another phase transition at 5°C).

C. Temperature Shift

Figure 7 shows the variation of the center of gravity of the spectrum with temperature in the range 25 to 900°C. The temperature shift arises because of the time dilation resulting from the motion of the emitting and absorbing nuclei. The shift in energy of radiation emitted by the source is

$$\Delta E/E = -\tfrac{1}{2}(\langle v_s^2\rangle_{\text{av}}/c^2),$$

where $\langle v_s^2\rangle_{\text{av}}$ is the mean square velocity of Fe^{57} nuclei in the source. Relative to the absorber the shift is

$$\Delta E/E = (1/2c^2)[\langle v_a^2\rangle_{\text{av}} - \langle v_s^2\rangle_{\text{av}}],$$

where a denotes the absorber. Since mean-square velocities are functions of temperature, it is often convenient to use a temperature coefficient defined by

$$(1/E)(\partial E/\partial T) = -(1/2c^2)(\partial/\partial T)\langle v^2\rangle_{\text{av}}.$$

If harmonic lattice forces are assumed, this expression becomes

$$(1/E)(\partial E/\partial T) = -C_L/2Mc^2, \qquad (1)$$

where M is the atomic mass and C_L is the specific heat of the lattice. In the high-temperature approximation, the coefficient becomes rigorously

$$(1/E)(\partial E/\partial T) = -3k/2Mc^2. \qquad (2)$$

The location of the center of gravity of the spectrum is plotted as a function of temperature in Fig. 7. The rather sharp break in the curve at T_c should be noted If the possibility of a temperature-dependent isomer shift is ignored, then, according to Eq. (1), the slope of the curve is proportional to the lattice specific heat at that temperature. Consequently, a break in the shift-versus-temperature curve indicates a specific-heat anomaly, which has been detected earlier by specific-heat measurements.[29,30] The slope of the curve at temperatures higher than 500°K is 2.0×10^{-15}/°K, which is close to the classical value given by (2).

IV. DISCUSSION

A. Electric Field Gradient

It may seem strange that 1% Fe-doped $BaTiO_3$ absorber gives a significantly larger quadrupole splitting (0.81±0.05 mm/sec) than 0.02% $Co^{2+}\rightarrow Fe^{3+}$ in the source lattice (0.46±0.03 mm/sec) at room temperature and, indeed, this fact raises a doubt as to which represents the EFG more accurately. We shall show in paper II that the Mössbauer measurements of the Fe-doped absorber relate to trivalent iron associated with a neighboring oxygen vacancy. In the Fe-doped $BaTiO_3$ absorber, the quadrupole splitting does not change significantly either with temperature or impurity concentration and, therefore, does not represent the true EFG. With a Co^{57}-$BaTiO_3$ source too, under certain conditions, one finds Fe^{3+} in a vacancy-associated environment yielding identical splitting and isomer shift. However, thermal quenching from high temperatures results mainly in a perfect local environment, so that the Mössbauer probe experiences the true crystalline EFG. The vanishing of the EFG, and particularly the close agreement between the experimentally determined and theoretically computed values of the EFG at room temperature, show that the Mössbauer probe can be successfully employed to study the solid-state properties of ferroelectric $BaTiO_3$. In addition, it shows that the iron impurity suffers the same displacement in the oxygen octahedron below T_c as the titanium ion. It is seen that the EFG follows closely the variation of P_s^2 with temperature. Rimai and DeMars[31] have shown

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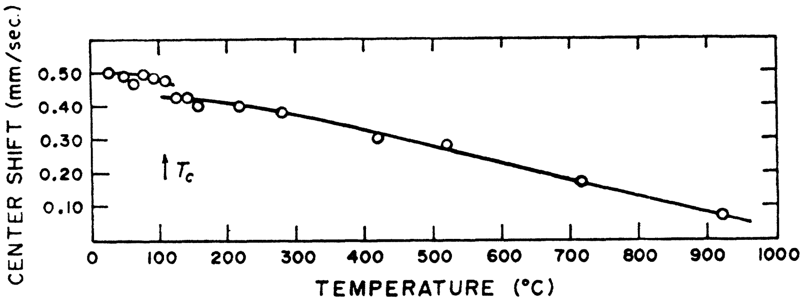

FIG. 7. Temperature shift in the spectrum of Fe^{57m}-BaTiO$_3$ source showing the jump in the slope of the curve at the Curie temperature T_c.

from paramagnetic-resonance studies that the axial field splitting parameter D for the S-state ion Fe^{3+} in BaTiO$_3$ also varies as P_s^2. It thus means that D varies linearly with the EFG or with A_2^0, the axial-term coefficient of the crystal-field potential, since

$$\mathrm{EFG}(q)=(1-\gamma_\infty)q_u=(1-\gamma_\infty)(5/\pi)^{1/2}A_2^0.$$

In this connection it is interesting to point out the observations of Müller *et al.*[32] on the nuclear quadrupole resonance (NQR) of Al^{27} in LaAlO$_3$ and the EPR of Fe^{3+} substituted at the Al site. They find that the field gradient for Al^{27} and D for Fe^{3+} are proportional to each other and also linearly dependent on the varying degree of lattice distortion in the temperature range 100–300°K.

The basic mechanisms responsible for the S-state splittings are not yet completely understood. Van Vleck and Penney[33] proposed a limited theory which demonstrated the possibility of ground-state splitting of an S-state ion due to high-order perturbations within the d^5 or f^7 configurations, or involving excited states of higher lying configurations and arising through admixed wave functions. Additional mechanisms[34] have been proposed, but all these have met with only partial success. Recently, a number of workers[35–37] have devoted attention to the relation between the parameters D of the phenomenological spin Hamiltonian and the coefficients A_2^0 and A_4^0 of the axial and cubic terms of the crystal-field potential:

$$V_{\mathrm{crys}}=A_2^0r^2Y_2^0+A_4^0r^4[Y_4+(5/14)^{1/2}(Y_4^4+Y_4^{-4})]+\cdots.$$

However, there seems to be no general agreement either in the experimental results or the theoretical conclusions. The present results indicate—at least to a first approximation—a linear relation between D and V_{ax}.

B. Temperature Shift

The isomer shift at room temperature referred to stainless steel is 0.50±0.02 mm/sec, and using the systematics referred to above one finds that the BaTiO$_3$ lattice as probed by Fe^{57} is partially ionic. Indeed, partial ionicity of the lattice has been assumed since early days by von Hippel,[38] Megaw,[39] and others to explain ferroelectricity in BaTiO$_3$. Recently, Russian workers[3] have shown from their studies of K x-ray absorption and emission spectra that the effective charges at the lattice sites are less than those inferred on the basis of an ionic model. Kinase and Takahasi[23] calculated spontaneous deformation in terms of the displacement of the Ti ion assuming the charge on the ion to be 4*e*. To explain the observed spontaneous polarization, it is then necessary that Ti ions have a displacement of 0.657 Å within the oxygen octahedra. However, this is much too large compared with that reported by Evans (0.156 Å) from x-ray diffraction measurements.[40] The authors argue that to obtain the observed spontaneous deformation for the reported displacement, it is necessary that the charge on the Ti ion be 2.06*e*, or, in other words, the degree of ionicity should be roughly 50%. This estimate agrees reasonably well with that inferred from our Mössbauer studies.

As $T\rightarrow\infty$, the relativistic part of the temperature coefficient must approach $3k/2Mc^2=2.44\times10^{-15}$ per °K. The experimental value at higher temperatures is slightly below the classical limit.

The transition from the tetragonal to the cubic phase occurs at about 107°C, at which the relativistic shift has substantially attained its classical value given by $\langle v^2\rangle_{\mathrm{av}}=3kT/M$. Therefore, it is not possible to account for the increase in the temperature shift (0.06 mm/sec) at the Curie temperature by any reasonable jump in the relativistic shift. If, instead, it is attributed to the isomer shift, the sense indicates again an increase in the electron density in going above the Curie temperature. In other words the results indicate a change in the covalent binding above T_c. In this connection it is interesting to note that Megaw[39] and Orgel[41] have attempted to explain the ferroelectric transition in terms of the change in the magnitude and angle of covalent bonding.

The discontinuity in the temperature shift at T_c

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indicates an anomaly in the specific heat. Such an anomaly has been reported by Todd and Lorenson[29] and Shirane and Takeda[30] from heat-capacity measurements.

C. Lamb-Mössbauer Factor

Several phenomenological theories have been advanced to explain the occurrence of ferroelectricity and antiferroelectricity in perovskites. These have mainly relied upon the existence of multiple minima in the free-energy function, nature of the chemical binding, electronic polarization, etc.[1] Recently, Cochran[8] and also Anderson[9] have explained the occurrence of the ordered phase below the Curie temperature by suggesting that the lattice becomes unstable towards one of the transverse-optical modes (wave vector $\mathbf{k}=0$). According to them it is sufficient if this anomalous mode is temperature-dependent. An essential point in Cochran's theory is that this mode can be expressed as

$$\omega_{\mathrm{an}}^2=\gamma(T-T_c). \tag{3}$$

It is then easy to explain the dependence of the static permittivity ϵ_s and also the Curie-Weiss law through the relation

$$\epsilon_s/\epsilon_e=\prod_{\alpha=1}^{N-1}(\omega_\alpha)_L^2/(\omega_\alpha)_T^2,$$

where ϵ_e is the permittivity measured at optical frequencies, $(\omega_\alpha)_L$ and $(\omega_\alpha)_T$ are the frequencies of the longitudinal- and transverse-optical modes for $\mathbf{k}=0$, and N denotes the number of ions in the unit cell. According to Cochran the long-range Coulomb interactions act in the anomalous optical mode against the short-range forces and give the dependence (3). Measurements of the nonelastic scattering of slow neutrons[42] and optical measurements in the far infrared region[43] carried out on $SrTiO_3$ confirm the assumed dependence. The numerical calculations of the normal frequencies of $BaTiO_3$ [44] and $SrTiO_3$ [45] lattice show that the relation is valid in the temperature region above T_c.

Taking into consideration Lipkin's sum rule,[46] it follows qualitatively that such a temperature-dependent mode will be reflected in the Lamb-Mössbauer measurements near T_c. Muzikar *et al.*[47] have analyzed the problem in some detail and have come to a similar conclusion. Therefore, the observed[48] anomalous variation of f near T_c is suggestive of the existence of a temperature-dependent mode as envisaged by Cochran.

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