Perturbed Directional Correlation of ^{44}Sc in Lead Titanate[†]

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(Received 2 November 1970)

Measurements of the perturbed γ-γ directional correlation have been made for the first excited state of ^{44}Sc in polycrystalline lead titanate at room temperature. A static electric quadrupole perturbation was observed, having an interaction strength $|QV_{zz}| = (3.92 \pm 0.05) \times 10^{-8}$ V. Using a recently reported value for the quadrupole moment of the ^{44}Sc first excited state, the electric field gradient at the Sc-ion site is found to be $V_{zz} = (2.2 \pm 0.4) \times 10^{21}$ V/m^2. The time-differential attenuation coefficient shows possible effects of a normal probability distribution for the field gradient with a relative width $\delta = 0.02$. No evidence of rhombic fields was found. A comparison of these results with earlier studies of ^{44}Sc in BaTiO$_3$ shows the electric field gradient at the Sc-ion site in PbTiO$_3$ to be larger than in BaTiO$_3$ by a factor of 1.46 ± 0.07.

I. INTRODUCTION

The technique of perturbed γ-γ directional correlations has become useful in obtaining information on internal fields and their symmetries for various materials including metals,[1] dielectrics,[2] and, most recently, macromolecules.[3,4] We wish to report here the application of this technique to the investigation of internal fields at the titanium-ion sites in ferroelectric lead titanate at room temperature. The nuclide chosen for this work is ^{44}Ti, which decays by electron capture to ^{44}Sc. The long parent lifetime, relatively long intermediate-level lifetime, and intermediate-level spin of 1 make ^{44}Sc an ideal nuclide for use in perturbed γ-γ directional correlations. In addition, the ^{44}Ti is expected to occupy regular lattice sites in lead titanate.

II. APPARATUS AND MEASUREMENTS

The time dependence of the directional correlation function of the 78–68 keV cascade in ^{44}Sc was examined using a two-detector time-differential coincidence system with crossover-pickoff timing and nominal time-to-pulse-height converter spans of 1 and 2 μsec. The detectors consisted of NaI crystals 1.5 in. in diameter and 0.5 in. thick mounted on Amperex No. 56 DVP photomultiplier tubes.

Because the detectors could not resolve the 78- and 68-keV photopeaks, both sides of the coincidence system were set to examine the unresolved peak between 50 and 100 keV. A delay was inserted in one side of the coincidence system so that prompt coincidences would correspond to half-maximum output pulses from the time-to-pulse-height converter. The accidental coincidence rate was determined by using two separate sources of ^{44}Ti activity and was subtracted from all spectra. Calibration of the time-to-pulse-height converter was achieved by using a pulse generator and known delay lines.

Since the intermediate-level spin of ^{44}Sc is 1, the directional correlation function has the simplified form

$$W(\theta, t) = 1 + A_{22}(t) P_2(\cos\theta), \qquad (1)$$

and is found experimentally by measurement of the anisotropy, given by

$$A(t) = [W(\pi) - W(\tfrac{1}{2}\pi)]/W(\tfrac{1}{2}\pi). \qquad (2)$$

Coincidence counts were taken over 4000-sec intervals at relative detector angles of 90, 180, 270, and 180 deg. The data from 90 and 270 deg and those from 180 deg were stored in alternate memory halves of a 256-channel multichannel analyzer and read out to a teletype for computer calculations of the channel-by-channel anisotropy.

The average anisotropy as a function of time was then obtained by folding together the symmetric halves of the channel-by-channel anisotropy about zero time delay. These data were then averaged over the time resolution of the coincidence system.

In order to obtain the time-differential attenuation coefficient $G_{22}(t)$ in a perturbed directional correlation experiment, the unperturbed coefficient $A_{22}(0)$ must be found, since

$$G_{22}(t) = A_{22}(t)/A_{22}(0). \qquad (3)$$

The unperturbed coefficient $A_{22}(0)$ for the 78–68-keV cascade was measured using a dilute liquid source in which Brownian motion minimizes the effects of any perturbing fields. The source used was 1 μCi of ^{44}Ti in 0.4 cm^3 of 6N HCl. This acidity was chosen to eliminate any effects of hydrolysis. The source was placed in a glass cylinder having an inner diameter of 0.21 cm and a length of 6.4 cm. The cylinder was positioned at a distance of 5.0 cm from the detectors.
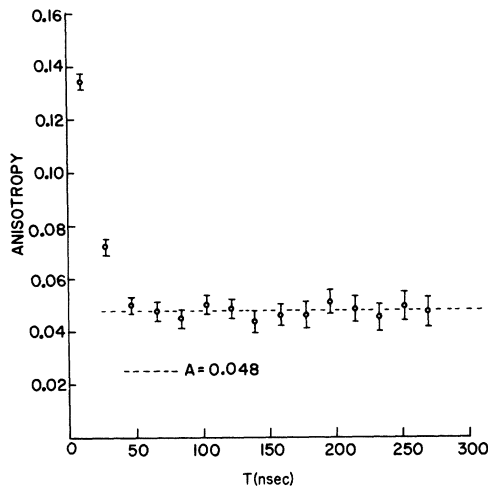
FIG. 1. Time-differential anisotropy of the ^{44}Sc cascade observed using ^{44}Ti in 6N HCl. Data are uncorrected for finite solid angle.

For the perturbed experiment, a sample of polycrystalline $PbTiO_3$ containing ^{44}Ti was obtained commercially. Oxides of lead and titanium were mixed together[5] and fired to 700 °C three times. The product was then pulverized and washed several times with acetic acid in order to remove unreacted excess PbO. An inactive sample of the source material was examined with a powder camera and found to be tetragonal $PbTiO_3$ with no detectable impurities. The sample had a specific activity of 0.7 μCi/mg of Ti and a total activity of 5.1 μCi. The resultant source was housed in a cylindrical glass capillary with an inner diameter of 0.12 cm and a length of 1.0 cm. This source was placed 7.0 cm from the detectors.

III. RESULTS

The anisotropy for the liquid source in the unperturbed experiment is shown in Fig. 1. The data points are uncorrected for the finite solid angle of the detectors. The initial peak is due to annihilation radiation associated with the positron decay of the ^{44}Sc ground state, and yields the time resolution of the coincidence system. The anisotropy is found to be independent of delay time T out to 285 nsec and has a solid-angle corrected value of 0.059 ± 0.001, which agrees well with previously published results.[6]

The observed time-dependent anisotropy of the $PbTiO_3$ source at room temperature is shown in Fig. 2. These data are corrected for finite solid angle. The anisotropy is clearly depressed below the unperturbed value indicated by the dotted line, and appears to be an oscillatory function of time. Such a behavior indicates an interaction between

the 1+ first excited level of ^{44}Sc and some static field at the scandium-ion site. Since $PbTiO_3$ is tetragonal at room temperature, an axially symmetric electric field gradient at the titanium-ion site is expected, which can interact with the electric quadrupole moment of the intermediate level of ^{44}Sc.

The experimental time-differential attenuation coefficient for the $PbTiO_3$ source can be calculated from the coefficients $A_{22}(0)$ and $A_{22}(t)$, and is shown in Fig. 3. Three distinct maxima and minima are visible. Near the 600-nsec delay the ratio of real to accidental coincidences is 0.25, and the apparent behavior of the attenuation coefficient has little meaning. For a static electric quadrupole interaction and an intermediate-level spin of $I = 1$, the time-differential attenuation coefficient has the form[7]

$$G_{22}(t) = \tfrac{3}{5} + \tfrac{2}{5}\cos\omega_0 t,\qquad(4)$$

where ω_0 is the fundamental interaction frequency. Since scandium is an impurity in the lead titanate lattice, it might be reasonable to expect a variation of the electric field gradient from nucleus to nucleus. Such a variation results[8] in a damping of the attenuation coefficient, since it must be integrated over a distribution of interaction frequencies. If we assume a normal distribution for the field gradient, the frequency-averaged time-differential attenuation coefficient is

$$G_{22}(t) = \tfrac{3}{5} + \tfrac{2}{5}e^{-\delta^2\omega^2 t^2/2}\cos\omega_0 t,\qquad(5)$$
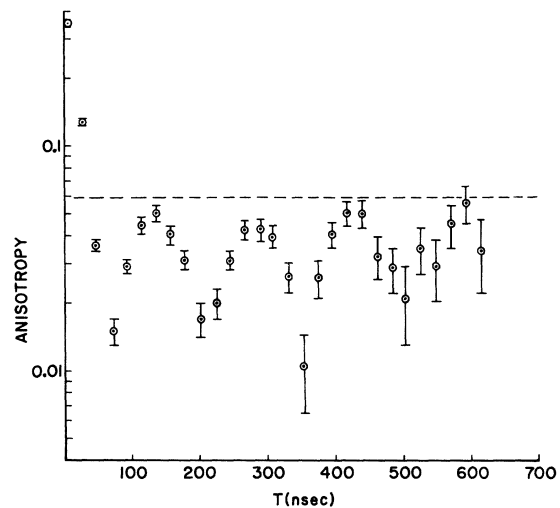

FIG. 2. Time-differential anisotropy of the ^{44}Sc cascade observed using the polycrystalline lead titanate source. Data are corrected for finite solid angle, with the unperturbed anisotropy being indicated by the dashed line.
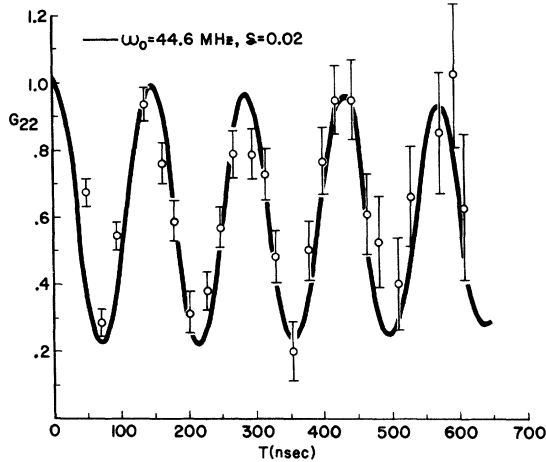
FIG. 3. Time-differential attenuation coefficient $G_{22}(T)$ from the lead titanate data. The solid curve is the theoretical $G_{22}(T)$ for $I = 1$ assuming a fundamental interaction frequency of 44.6 MHz and a normal distribution for the electric field gradient with a relative width of $\delta = 0.02$.

where δ is the relative width of the distribution.

A least-squares fit to our experimental data with a theoretical curve corrected for finite time resolution is shown in Fig. 3. The minimum least-squares sum was 44.9. This gives $\delta = 0.02$ with upper and lower limits of 0.00 and 0.03, and a fundamental interaction frequency $\omega_0 = 44.6 \pm 0.5$ MHz. This corresponds to an interaction strength $|QV_{zz}| = (3.92 \pm 0.05) \times 10^{-8}$ V. Within the accuracy of the data, it is very likely that all ^{44}Sc nuclei see the same electric field gradient.

As a check on the calibration of the time-to-pulse-height converter, the intermediate-level lifetime of ^{44}Sc was calculated using all coincidence spectra and was found to be 152 ± 4 nsec. This agrees well with previously published results.[6]

Since the annihilation radiation due to the positron decay of the ^{44}Sc ground state manifests itself in a large positive anisotropy, care must be taken not to include it in the attenuation coefficient. The first data point at 50 nsec, and probably the second one at 70 nsec, still contains small amounts of annihilation radiation and thus does not lie on the theoretical curve.

The quadrupole moment of the 68-keV level in ^{44}Sc has recently[9] been calculated, based on directional correlation[10] and Mössbauer[11] measurements in BaTiO$_3$. It is found that $Q = 0.18 \pm 0.03$ b. Using this value, we obtain $V_{zz} = (2.20 \pm 0.40) \times 10^{21}$ V/m^2 as the electric field gradient at the scandium site in PbTiO$_3$ at room temperature.

As mentioned earlier, the field at the titanium-ion site is expected to be axially symmetric since

PbTiO$_3$ is tetragonal at room temperature. This is shown experimentally by the value of the time-integrated attenuation coefficient, which depends strongly on the presence of rhombic fields. Tabulated limiting values of the time-integrated attenuation coefficient $\bar{G}_{22}(\infty)$ as a function of the asymmetry parameter η show that, for $I = 1$, $\bar{G}_{22}(\infty)$ drops from 0.6 to 0.4 as η increases from 0 to 0.2. The experimental time-integrated attenuation coefficient was obtained by numerical integration of the data over 440 nsec and gives $\bar{G}_{22}(440 \text{ nsec}) = 0.64 \pm 0.05$. This compares well with the theoretical value of $\bar{G}_{22}(440 \text{ nsec}) = 0.61$ for an axially symmetric static electric quadrupole interaction.

IV. DISCUSSION

Recent work[12] has shown that the maximum energy available for the K-electron capture decay of the ^{44}Ti ground state is 272 keV. Using this value, the recoil energy of the titanium nucleus is found[13] to be 0.9 eV. The scandium ions are thus expected to occupy the original titanium-ion sites. This should also be true for previous work[2] done on BaTiO$_3$. A comparison between the electric field gradients at the scandium-ion sites in lead titanate and barium titanate may then be made. The field gradient in lead titanate is larger by a factor of 1.46 ± 0.07.

In the work on BaTiO$_3$, a $\delta = 0.25$ was reported, and it was argued that this was due to motion of the scandium impurity during the 50-μsec half-life of the ^{44}Sc second excited level. The small δ we observed for PbTiO$_3$ suggests an alternate explanation for the large δ. The barium titanate source consisted[14] of very large grains with major diameters ranging from 20 to 2000 μ. In our work the source was a fine powder with grains ranging in size from 0.033 to 0.33 μ across. We suggest that the large δ observed with barium titanate is due to the presence of large nonuniform stresses incurred during growth of the crystallites. With better annealing, as in our finely pulverized lead titanate source, fewer of these stresses are present. The fact that the observed interactions in both barium titanate and lead titanate are axially symmetric indicates that any nonuniform stresses present in these crystals are along the polar axis.

ACKNOWLEDGMENTS

†Work supported in part by the Research Corporation, Chicago, Ill.

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[1] H. Albers-Schonberg, E. Herr, T. B. Novey, and P. Scherrer, Helv. Phys. Acta 27, 547 (1954).

[2] J. C. Glass and J. K. Kliwer, Nucl. Phys. A115, 234 (1968).

[3] C. Meares, R. Bryant, J. Baldeschwieler, and D. Shirley, Proc. Natl. Acad. Sci. U. S. 64, 1155 (1970).

[4] J. C. Glass and G. Graf, Nature 226, 635 (1970).

[5] New England Nuclear Corp. (private communication).

[6] R. Ristinen and A. Sunyar, Phys. Rev. 153, 1209 (1967).

[7] R. M. Steffen, Advan. Phys. 4, 294 (1955).

[8] E. Matthias, W. Schneider, and R. Steffen, Phys. Letters 4, 41 (1963).

[9] L. F. Bertain and J. K. Kliwer, Bull. Am. Phys. Soc. 14, 1233 (1969).

[10] L. F. Bertain, Ph. D. thesis (University of Nevada, 1970) (unpublished).

[11] V. G. Bhide and M. S. Multani, Phys. Rev. 139, A1983 (1965).

[12] J. J. Simpson, W. R. Dixon, and R. S. Storey, Phys. Letters 30B, 478 (1969).

[13] C. S. Wu and S. A. Moszkowski, Beta Decay (Interscience, New York, 1966), p. 196.

[14] L. F. Bertain and J. K. Kliwer (private communication).

t-Matrix Analysis of the Magnetic Phases of a Narrow Energy Band

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(Received 7 January 1971)

Previous calculations of a t-matrix approximation to Hubbard's model of a half-filled narrow energy band are extended to cover all possible occupancies. The method is exact in the low-density limit. The paramagnetic state is found to be more stable than in the Kanamori approximation. The nearly half-filled band, infinite-repulsion limit is also consistent with Nagaoka's prediction. The resulting phase transitions between paramagnetic, ferromagnetic, and antiferromagnetic states occur at smaller bandwidth/potential-energy ratios than those of Penn's Hartree-Fock approach.

I. INTRODUCTION

The authors have previously investigated the ground state of a half-filled nondegenerate narrow energy band using second-order perturbation theory.[1] This was compared to a t-matrix approximation. The electronic Hamiltonian used was that of Hubbard,[2] and the calculations were performed assuming a simple-cubic lattice in the tight-binding limit.

In the weak-interaction limit, an expansion in the bare interaction or the reaction matrix is convergent. Such expansions are, however, generally known to be unreliable for a paramagnetic state at larger carrier densities and for a strong electronic interaction. These considerations are fully expanded on in our earlier paper.[1] But it turns out that, for the half-filled band in the Hubbard model, the paramagnetic state becomes unstable in favor of an antiferromagnetic state before the strength of the interaction can invalidate either approximations. Most of the correlation is already included in this long-range-ordered state since opposite-spin electrons effectively stay out of each other's way. Although it was found that a t-matrix approximation is uncalled for in the half-filled-band case, it is necessary in the low-carrier-density limit. As shown by Day[3] the t-matrix approximation is the first term in a power-series expansion in the density and thus exact at low electron or hole occupancies. It then appears worthwhile at this stage to extend the t-matrix calculations to cover all band densities. The resulting paramagnetic, ferromagnetic, and antiferromagnetic phase study will be accurate at low density or larger bandwidths. The only questionable results would be those for large occupancies and large repulsion.

All calculations will again be performed for a simple-cubic structure in the tight-binding limit at absolute zero of temperature. The interatomic distance is normalized to 1.