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# Temperature-Dependent Optical Mode in Antiferroelectric $PbZrO_3$ by the Mössbauer Effect

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The Mössbauer effect for $Sn^{119m}$ in the $PbZrO_3$ lattice has been studied from 27 to 320 °C, with particular emphasis on the region near the Curie temperature. The Mössbauer fraction changes by $(40 \pm 8)\%$ at the transition temperature $T_C$ from its value at room temperature. This is to be compared with the corresponding change of 10% for the earlier ferroelectric $BaTiO_3 : Sn^{119m}$ system. These results are consistent with Dvorak's suggestion that in antiferroelectrics the frequency over the entire optical branch may vanish at $T_C$. A sharp change in the isomer shift and the vanishing of the electric field gradient has also been observed, as is expected from the change in the crystal structure at $T_C$.

## I. INTRODUCTION

Ferroelectricity in perovskite-type crystals such as $BaTiO_3$ and $SrTiO_3$ has lately been a subject of considerable experimental investigations by means of various techniques: the Mössbauer effect,[1] neutron scattering,[2] and dielectric-constant measurements.[3] The main reason for this increased activity has been the theory of Cochran, who describes ferroelectricity in these crystals as being due to the occurrence of instabilities in the lattice-dynamical modes (particularly the optical modes) at the ferro-to-para transition temperature.[4] In fact, it has been suggested that $\omega_T^2 \propto (T - T_c)$, where $\omega_T$ is the frequency of the transverse optical mode at $K = 0$, and $T_C$ is the transition temperature. Such a behavior of $(\omega_T^2)_{K=0}$ near the transition temperature has been verified in $SrTiO_3$ by studies of neutron scattering,[2] and in $Co^{57}$-doped $BaTiO_3$ by the Mössbauer effect.[1]

It has recently been suggested that in antiferroelectrics the entire optical branch may be temperature dependent near the transition temperature, in contrast with ferroelectrics, where only the long-wave part ($K=0$) of the optical branch is temperature dependent.[5] The behavior for the temperature-dependent frequency of the transverse optical modes in antiferroelectrics is expected to be of the form[6]

$$\omega_T^2(K)=\gamma\{T-[T_C+\Delta T(K)]\} . \qquad (1)$$

For an antiferroelectric crystal, $\Delta T(K)$ is thought to have its maximum value for $K$ at the edge of the Brillouin zone; with decreasing $K$ it decreases and finally becomes zero for $K=0$. It was, therefore, considered of interest to investigate the antiferroelectric $PbZrO_3$ by the Mössbauer technique.

## II. EXPERIMENTAL

The symmetry of the antiferroelectric phase in $PbZrO_3$ is orthorhombic, and it undergoes a phase transition to the cubic phase at 230 °C. The detailed crystal structure has been investigated by x-ray and neutron scattering techniques by Sawaguchi *et al.*[7]

In our study of $PbZrO_3$ we have employed $Sn^{119}$ as a Mössbauer probe. Tin enters into the $PbZrO_3$ lattice, replacing $Zr^{4+}$ in the tetravalent state. Thus the difficulties due to local charge-compensating vacancies that are present in the earlier Mössbauer studies of $Co^{57}$ in systems like $BaTiO_3$ are absent here.

$PbZrO_3$ was ground to a fine powder pressed into a thin tablet and sintered at 1050 °C. About 100 $\mu$Ci activity of $Sn^{119}$ in the form of an aqueous solution of $Sn^{119}Cl_2$ was allowed to evaporate from a clean surface of $PbZrO_3$ tablet, and the residue was diffused inside by heating the tablet in a hydrogen atmosphere at 1000 °C. For removing the effects arising out of the possible vacancies created by hydrogen, a final heat treatment in air atmosphere was carried out at the same temperature. A $PbZrO_3:Sn^{119m}$ source, when matched with a PdSn absorber containing about 10% (atomic Sn), gave a full width at half-maximum of 0.95 mm/sec at room temperature (300 °K).

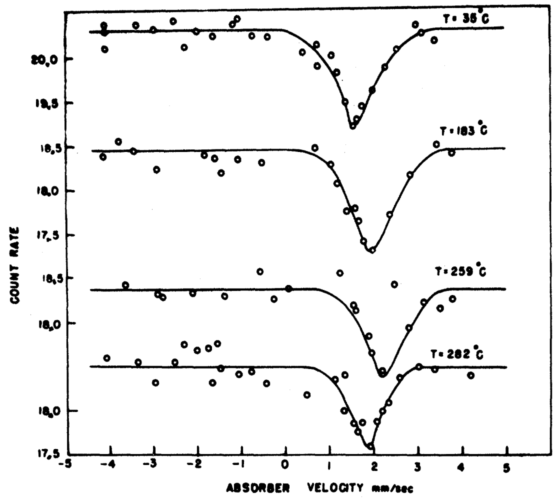

FIG. 1. Typical spectra for $PbZrO_3:Sn^{119*}$ at various temperatures.

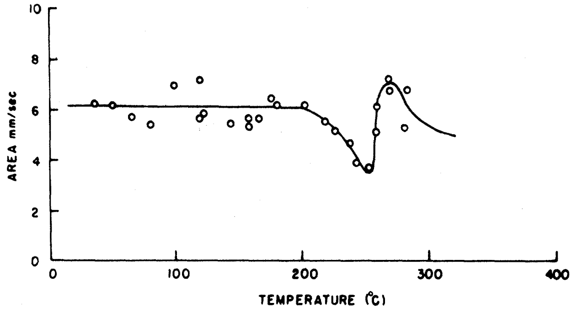

FIG. 2. Temperature variation of the normalized area, exhibiting the anomaly in the vicinity of the Curie temperature $T_C$.

Mössbauer data were collected in transmission geometry using a PdSn absorber and $PbZrO_3:Sn^{119m}$ as a source to which the linear velocity was imparted by the constant-velocity mechanical drive. The radiation was detected by a RCA 6810A photomultiplier coupled with 1-mm-thick NaI:Tl scintillator. A total of $2.0\times10^4$ counts for each velocity setting were recorded. The source was put on a copper disk, and the Mössbauer spectra at various temperatures below and above $T_C$ were taken by heating the source in a suitably designed furnace in which the temperatures could be uniformly maintained within ± 1 °C.

## III. RESULTS

The Mössbauer spectra at various temperatures are shown in Fig. 1. The observed isomer shift at room temperature is the same as that of $SnO_2$ with respect to PdSn absorber, from which it can be inferred that the Sn in $PbZrO_3$ replaces Zr in tetravalent state. The full width at half-maximum of the lines below $T_C$ are larger than that observed for $PdSn^{119m}$ source against the same PdSn absorber, while above $T_C$ the lines are narrower (Fig. 3). This could be interpreted as being due to the presence of a weak quadrupole interaction arising from the orthorhombic character of $PbZrO_3$ below $T_C$. We shall explain later the magnitude of the quadrupole splitting in terms of the electric-field-gradient calculations from the known crystal structure of $PbZrO_3$.[7]

The strength of the resonance absorption can be obtained from the area $A$ above the measured dips, normalized to unity off resonance. Figure 2 shows the variation with temperature of the measured area. It is interesting to see that as one approaches $T_C$, the area under the resonance curve decreases rather sharply, reaches a minimum at $T_C$, and then rises and falls gradually later on.

The observed variation in Fig. 2 is indicative of the existence of a strong temperature-dependent transverse optical mode in $PbZrO_3$, in conformity with the theoretical prediction of Cochran. We can also obtain from Fig. 2 the relative change in the area at the transition temperature normalized to the area at room temperature. The area at any temperature as in Fig. 2 is dependent on the various background effects present in the experiment (including the most important, the nonresonant background), but the normalized relative area is independent of any such effect. One can also deduce the corresponding value from the earlier Mössbauer studies of Ba(Ti-Sn)$O_3$ system.[8] A comparison of the two shows that antiferroelectric $PbZrO_3$ shows a change of Mössbauer fraction by $(40 \pm 8)\%$ at the transition temperature as compared with 10% for the ferroelectric $BaTiO_3$. Dvŏrak suggested that in antiferroelectrics the frequency over the entire transverse optical branch may be damped out at the transition temperature, producing a bigger effect in antiferroelectrics than in ferroelectrics.[5] Our results above are in agreement with this suggestion. Neutron scattering studies of $PbZrO_3$ are suggested from which one can directly obtain the temperature dependence of $\omega_K$ for various values of $K$ in the Brillouin zone. Such experiments, however, may be difficult to carry out because of the large scattering cross section of Pb in $PbZrO_3$.

There could also be a change in $\Theta_D$ in $PbZrO_3$ as we pass through the transition temperature, due to the piezoacoustic coupling. However, because of the limited data available above $T_C$ and the imperfect knowledge of the background in the above area calculations, such an analysis is not possible.

From the experimentally observed broadened line at room temperature we have obtained an estimate of the quadrupole splitting, using a linewidth of 0.8 mm/sec, which is the same as that measured in a study of $PdSn^{119m}$ source with the same PdSn absorber. Our value for the splitting is 0.2–0.3 mm/sec. For the $\frac{3}{2}^+$ state of $Sn^{119}$ nucleus the quadrupole splitting is given by

$$\Delta E = \tfrac{1}{2}(eq)(eQ) , \qquad (2)$$

where $eq$ is the electric field gradient, and $Q$ is the quadrupole moment for the $\frac{3}{2}^+$ state of the $Sn^{119}$ nucleus. The ionic electric field gradient $q$ is given by $q = q_L(1-\gamma_\infty)$, where $q_L$ is the field gradient at Sn nucleus due to the distortion of oxygen ions surrounding the Sn nucleus, and $\gamma_\infty$ is the antishielding factor for the $Sn^{4+}$ state of the Sn ion.[9] On the point-charge model, using nearest-neighbor oxygen atoms to the Sn ion and the crystal structure as given by Sawaguchi *et al.*,[7] we have calculated for $PbZrO_3$, $eq_L = 2.3 \times 10^{13}$ esu/cm$^2$. Assuming $Q$ for $Sn^{119}$ to be 0.07 b,[10] and $\gamma_\infty = -10$ for the $Sn^{4+}$ state in $PbZrO_3$,[11] we get the ionic contribution to the splitting as $3 \times 10^{-2}$ mm/sec. To this one must add the dipolar contribution. It is difficult to evaluate this in $PbZrO_3$ because of its antiferroelectric nature. However, if we assume that it is the same order of magnitude as in $KNbO_3$,[12] then we get a net splitting due to the ionic displacement of about 0.1 mm/sec, which agrees well with our measured value of 0.2–0.3 mm/sec. The precise calculations of the splitting are, however, complicated by our inaccurate knowledge of $Q$ and $\gamma_\infty$. In addition, it is possible that the complete ionicity of Sn that we have assumed in the above calculation is not valid, as is suspected also in $SnO_2$.[13] In such a case, there will be an additional contribution from the unbalanced $5p$ electrons on the Sn atom and the antishielding effect produced by them.

Figure 3 shows the observed chemical shift and the full width at half-maximum of the observed spectra as a function of temperature. We see a sudden break in the chemical shift near the transition temperature. This could be for one or more of the following reasons: (i) a change in lattice

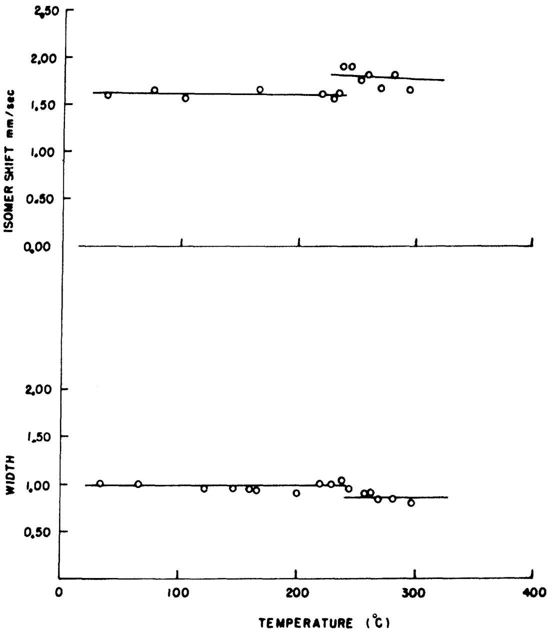

FIG. 3. Variation of the full width at half-maximum and isomer shift as a function of temperature.

specific heat $C_L$; (ii) a change in the isomeric shift due to the change in crystal structure; (iii) a change in the Debye temperature $\Theta_D$.

As mentioned earlier, the full width at half-maximum also undergoes a change near the transition temperature, as one expects from the vanishing of the electric field gradient in the cubic state of the crystal above.

Finally, it may be noticed from Figs. 2 and 3 that while the isomer shift and the width show a break at 236 °C, the minimum in the Mössbauer fraction occurs at a temperature ~254 °C. The transition temperature of $PbZrO_3$ is also 236 °C as determined by dielectric-loss measurements.[14] This suggests that the crystal phase change from cubic to orthorhombic, which affects both the isomer shift and the width, occurs at the transition temperature of 236 °C. The Mössbauer-fraction minimum occurs at a higher temperature because it is sensitive to modes for all values of $K$, while the dielectric-constant measurement is sensitive to the $K=0$ mode only. Silverman has calculated $(\Delta T)_K$ of Eq. (1) on a linear chain model of atoms, and has found a value of 45 °C for $\Delta T$, for $K$ lying near the edge of the Brillouin zone.[6] This would imply a minimum in the Mössbauer fraction at a temperature between 236 and 281 °C, which is in good agreement with our observed value of 254 °C.

Plotnikova *et al.*, have also carried out measurements on $PbZrO_3$ with a $Sn^{119}$ Mössbauer probe.[15] However, they do not observe any anomaly in the Mössbauer fraction at the transition temperature. In view of our observed effect in the same system and also of the earlier observed effects in $BaTiO_3$ doped with $Sn^{119}$ and $Co^{57}$, their results are difficult to understand.[1,8] It is possible that in their sample preparations Sn has not entered into $PbZrO_3$ and has remained as $SnO_2$ on the surface of the specimen. Since the isomer shift of Sn in $PbZrO_3$ is the same as that for $SnO_2$, it is not easy to distinguish between the two.

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