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James P. Canner

C. M. Yagnik

Robert Gerson

*Missouri University of Science and Technology*

William Joseph James

*Missouri University of Science and Technology*

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## Mössbauer-Effect Studies of the Phase Transitions in Antiferroelectric $\text{PbZrO}_3$ and Ferroelectric $\text{PbTi}_{0.02}\text{Zr}_{0.8}\text{O}_3$ †

James P. Canner,\* C. M. Yagnik,‡ R. Gerson, and W. J. James

*Departments of Physics and Chemistry and the Graduate Center for Materials Research, University of Missouri-Rolla, Rolla, Missouri 65401*

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The Mössbauer spectra were studied for the antiferroelectric compound  $\text{PbZrO}_3$  and for the closely related ferroelectric  $\text{PbTi}_{0.02}\text{Zr}_{0.8}\text{O}_3$ . In both cases, a substitution of 5-mol%  $\text{BiFeO}_3$  was made to permit the Mössbauer measurements. Little difference was found in the isomer shift in these compounds, whether they were in the ferroelectric, antiferroelectric, or cubic state, indicating that the bonding character is not affected by the transitions among the states. There was a pronounced and approximately equivalent dip in the recoil-free fraction at the Curie points of both the antiferroelectric and ferroelectric materials, associated with a low-frequency lattice mode at the Brillouin-zone boundary.

### INTRODUCTION

During the past few years, the Mössbauer effect has been used to study the temperature-dependent optical mode in ferroelectric crystals.<sup>1-5</sup> Recently, Jain *et al.*<sup>6</sup> have studied the Mössbauer effect in  $\text{PbZrO}_3$  as the material goes through its Curie point.  $\text{PbZrO}_3$  is generally classified as an antiferroelectric, although in fact the material has a spontaneous polarization, similar to that of a ferroelectric, but along an axis perpendicular to the plane containing the opposed antiferroelectric polarizations.<sup>7</sup> The space group in the antiferroelectric phase is  $Pba2$ , while that for  $\text{Pb}(\text{Ti}_{0.20}\text{Zr}_{0.80})\text{O}_3$  just below its Curie point is  $R3m$ . As originally suggested by Dvorak,<sup>8</sup> Jain found that the decrease in recoilless fraction was more severe for the antiferroelectric  $\text{PbZrO}_3$  than for previously measured ferroelectrics, an effect predicted on the basis that antiferroelectricity should be associated with a lowering of lattice-mode frequencies at the Brillouin-zone boundary. The boundary is a region in momentum space, where a low-frequency lattice mode would be particularly effective in lowering the recoil-free fraction.<sup>8</sup>

The present paper deals with Mössbauer-effect studies using  $^{57}\text{Fe}$  substituted in  $\text{PbZrO}_3$  and in a closely related ferroelectric.  $(\text{PbZrO}_3)_{0.95}(\text{BiFeO}_3)_{0.05}$  (hereafter designated PZ) and  $(\text{PbTi}_{0.20}\text{Zr}_{0.80}\text{O}_3)_{0.95}(\text{BiFeO}_3)_{0.05}$  (hereafter designated PTZ) are the two materials studied. Both have a perovskitelike structure, but the former has antiferroelectric properties while the latter is a ferroelectric. The main crystallographic and dielectric properties of the materials can be found in Ref. 9 and 10. It was observed that the 5-mol%  $\text{BiFeO}_3$  addition, made in the present study to permit Mössbauer spectroscopy does not greatly alter the properties of the base materials. Accordingly, the present work can be looked upon as a study of  $\text{PbZrO}_3$  and of  $\text{PbTi}_{0.2}\text{Zr}_{0.8}\text{O}_3$ , and the object is to determine whether there exists a major difference in Mössbauer spectra between a ferroelectric and an antiferroelectric whose chemical compositions do not differ greatly. A further object is to use  $^{57}\text{Fe}$  to study the quadrupole splitting in the materials, a measurement which was not feasible in the previous

studies involving  $^{119m}\text{Sn}$ . It should be noted that Biran *et al.*<sup>11</sup> have studied the Mössbauer effect in the system  $\text{PbZrO}_3\text{-BiFeO}_3$ , but for high concentrations of  $\text{BiFeO}_3$ .

### EXPERIMENTAL

As starting materials,  $\text{Bi}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{PbO}$ ,  $\text{TiO}_2$ , and  $\text{Fe}_2\text{O}_3$  enriched in  $^{57}\text{Fe}$  to 81.55% were mixed in stoichiometric proportions for several hours using a mechanical mortar and pestle. The PZ mixture was fired at 1100 °C for 1.5 h, whereas the PTZ mixture was sintered at 850 °C for 2 h. Both samples were air quenched, after which the solid solutions were checked, using x-ray diffraction for the completion of the reaction.

The Mössbauer spectra were obtained using an Austin Science Associates conventional spectrometer. The source used was  $^{57}\text{Co}$  (10 mCi) in a copper matrix. The source was maintained at room temperature during the course of all measurements and vertical transmission geometry was used. The absorbers were prepared by spreading the powder on a thin beryllium foil using acetone as a suspension medium. The absorbers were taken to high temperature in a short tube furnace.<sup>12</sup> The absorber temperature was monitored with a Chromel-Alumel thermocouple to  $\pm 3$  °C. The spectrometer was calibrated using natural iron foil at room temperature.

### RESULTS AND DISCUSSION

A typical Mössbauer spectrum for this system is given in Fig. 1. The spectra for other similar systems are given in Ref. 12. In both the PZ and PTZ systems, the Mössbauer spectra could be resolved into doublets, both above and below the Curie temperatures, with the linewidth being about 0.5–0.8 mm/sec. This large linewidth, fairly characteristic of solid solutions of this sort, is caused by the variety of crystalline environments of the trivalent  $^{57}\text{Fe}$  ion occupying a  $\text{Zr}^{4+}$  site, and having many possible bismuth-lead and zirconium-titanium-iron configurations in the neighboring cation sites. There was a slight symmetry in many of the doublet patterns of PZ. In powders of this sort, there is no

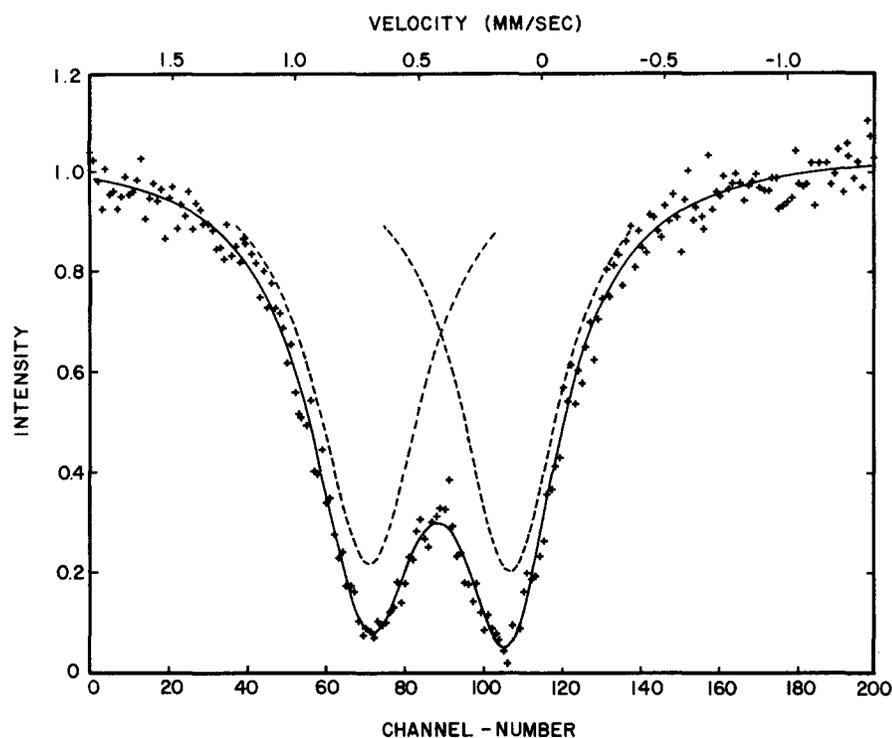


FIG. 1. Mössbauer absorption spectrum of PTZ,  $(\text{PbTi}_{0.20}\text{Zr}_{0.80}\text{O}_3)_{0.95}(\text{BiFeO}_3)_{0.05}$ , at room temperature. The source was  $^{57}\text{Co}$  in copper, and the zero of the velocity scale is the center of the spectrum of iron at room temperature.

reason to expect any preferred orientation, so the asymmetry is probably a minor Karyagin<sup>13</sup> effect.

*Isomer Shift:* At room temperature, the isomer shifts for the PZ and PTZ solutions were essentially identical (about 0.39 mm/sec, referenced to natural iron), indicating that there is almost no change in the ionicity of the bonding between the antiferroelectric and ferroelectric solid solutions. For both solid solutions, the relative changes in  $\gamma$ -ray energy with

temperature indicated by the curves in Fig. 2 were also equal (about  $-2.2 \times 10^{-15}/^\circ\text{K}$  and somewhat lower in magnitude than the value of  $-2.44 \times 10^{-15}/^\circ\text{K}$  found for a pure second-order Doppler shift. The slight difference between the values is probably associated with a small change in the geometry of the octahedral cage containing the iron as the temperature is raised. At the Curie point, both materials show only a very small irregularity in the isomer shift—temperature curves, indicating that the ioni-

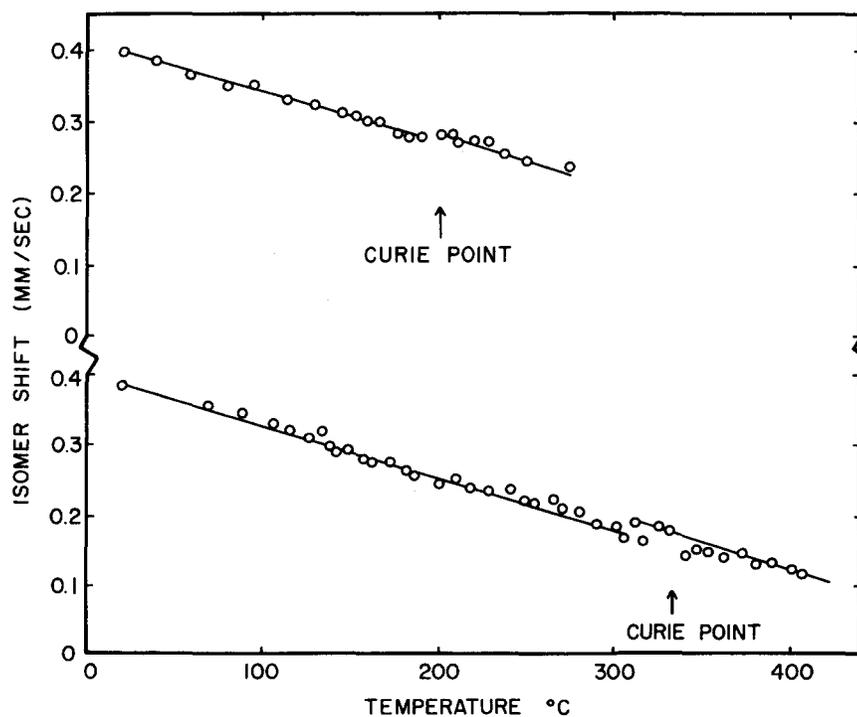


FIG. 2. Isomer shift as a function of temperature for PZ (upper curve) and PTZ (lower curve).

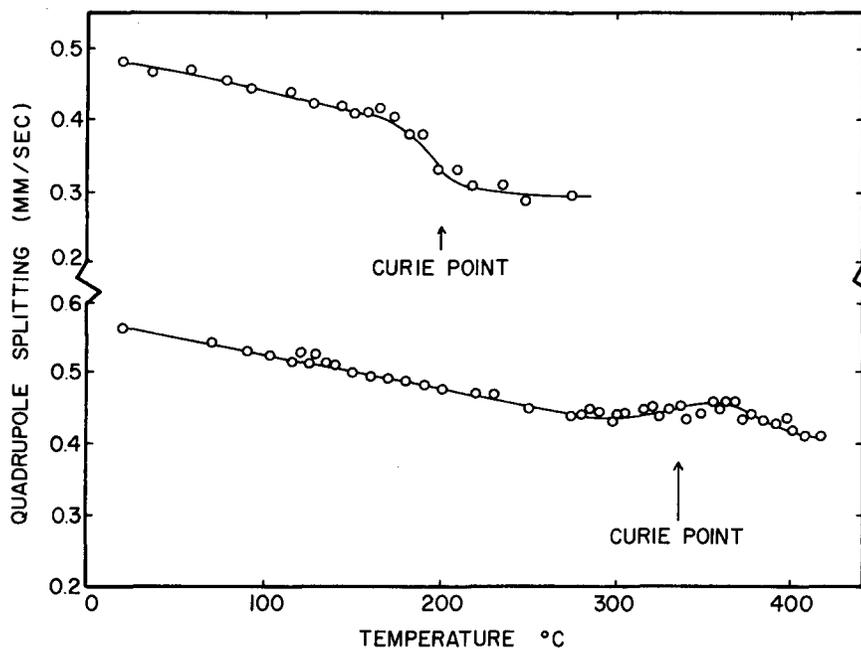


FIG. 3. Quadrupole splitting as a function of temperature for PZ (upper curve) and PTZ (lower curve).

cities of the cubic and ferroelectric or antiferroelectric phases are very nearly equal. All of these data show that the nature of the chemical bonding is essentially unaffected in this type of ferroelectric or antiferroelectric transition.

There is a possible question as to the correctness of analyzing the spectra obtained for isomer shift and quadrupole splitting in the usual way. Errors may occur in the interpretation if a considerable range of isomer shifts and quadrupole splittings are present simultaneously. In fact, the validity of the conventional analysis used in this experiment depends

on the limited range of isomer shift in these compounds, which are all very similar chemically.

One good indication that the calculated isomer shift is a valid one is the closeness of its temperature coefficient, for both of the materials studied, to the classical value. If there were a considerable dispersion of isomer shifts, changing as the lattice changed with temperature, this would be unlikely to occur. The behavior of the calculated isomer shift at the Curie temperatures is also self-consistent (there is only a small discontinuity, similar to that found by Jain *et al.*<sup>6</sup> for the substitution of  $^{119}\text{mSn}$

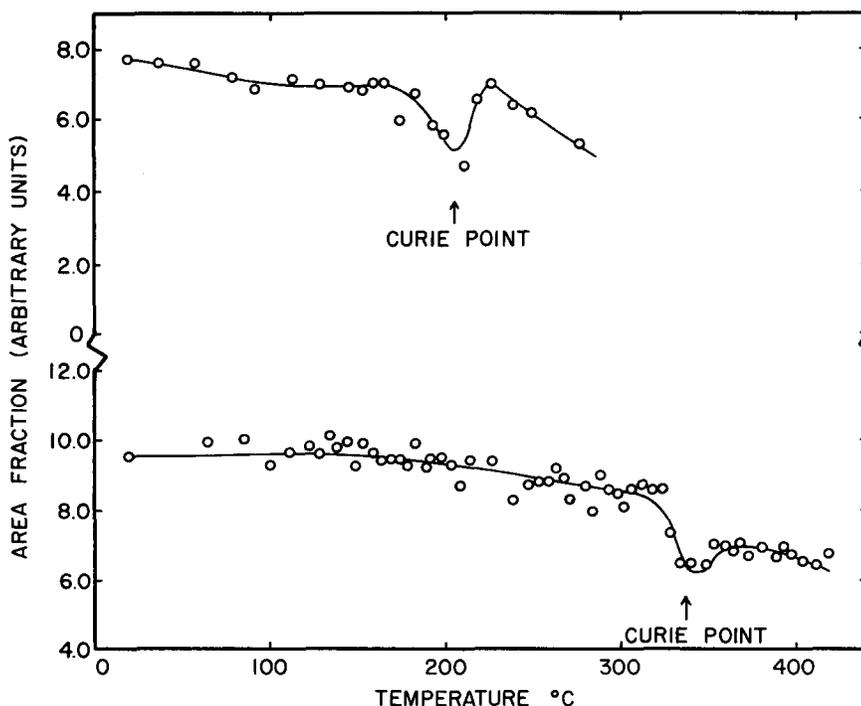


FIG. 4. Area fraction for recoil-free absorption for PZ (upper curve) and PTZ (lower curve).

in  $\text{PbZrO}_3$ ), although the quadrupole splitting behaves differently for the two materials, as one might expect. Finally, the isomer shifts for both the PT and PTZ compositions are essentially the same as that measured for the solid solution  $(\text{PbTiO}_3)_{0.95}(\text{BiFeO}_3)_{0.05}$  at room temperature,<sup>14</sup> again indicating a valid measurement of this quantity for chemically similar materials. The observed line-width of the Mössbauer absorption line (0.5–0.8 mm/sec) may thus be taken primarily to represent a range of quadrupole splittings, caused by nonuniform nuclear electric field gradients among atoms having about the same isomer shift. A similar assumption has been used successfully by Bell<sup>15</sup> to analyze Mössbauer data in another perovskitic system.

**Quadrupole Splitting:** Both PZ and PTZ show a strong quadrupole splitting at room temperature. The spectra were analyzed on the basis of two peaks, but it must be remembered that these are superpositions of the effects due to many electronic and nuclear environments, so that the measured quadrupole splitting is in fact an average. The electric field gradient, which causes the splitting, is traceable to two causes. The first of these is the ferroelectric (or antiferroelectric) distortion, which displaces the  $^{57}\text{Fe}$  from a symmetric lattice position. The second cause, which operates even when no ferroelectric effect is present (above the Curie point, for example), is the nonsymmetric distribution of  $\text{Pb}^{2+}$  and  $\text{Bi}^{3+}$  ions on one site and  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$ , and  $\text{Fe}^{3+}$  on another. In a ferroelectric (or antiferroelectric) the two causes are not independent. The field due to a  $\text{Bi}^{3+}$ - $\text{Fe}^{3+}$  dipole (substituting for  $\text{Pb}^{2+}$ - $\text{Zr}^{4+}$ ) will polarize the lattice, even in the paraelectric state, and affect the direction and magnitude of the ferroelectric polarization during a transition.

Referring to Fig. 3, it is seen that in the ferroelectric (or antiferroelectric) phase the quadrupole splitting decreases with increasing temperature below the Curie point. At the Curie point, the quadrupole splitting decreases sharply for PZ, but not for PTZ, and above the Curie point it is relatively constant and not due to ferroelectricity.

Apparently, in the PTZ composition the field gradient at the  $^{57}\text{Fe}$  site is not greatly changed at the Curie point. It is to be expected that most of the  $^{57}\text{Fe}$  nuclei will be paired with a Bi ion, substituted in one of the neighboring Pb sites, since this minimizes the electrical energy of the lattice. This arrangement generates a local polarization along the body diagonal of the perovskite unit cell. In the ferroelectric phase, which is rhombohedral in symmetry, the ferroelectric polarization is also along the body diagonal. The constancy of quadrupole splitting at the Curie point indicates that much of the ferroelectric polarization, in these materials which have very small polarization domains, tends to coincide with the dipole moment due to Bi-Fe substitution. This is

not the case for antiferroelectric PZ, as it is orthorhombic; therefore, the electric dipole moment cannot be in the same direction as the substitutional dipole moment. This has been shown previously to be the situation for the compound  $(\text{PbTiO}_3)_{0.95}(\text{BiFeO}_3)_{0.05}$  which is tetragonal in the ferroelectric state.<sup>5</sup>

**Recoilless Fraction:** Figure 4 shows the area fraction of radiation absorbed recoillessly for the PZ and PTZ powders. The relative drop in recoilless fraction at the Curie point is about 30% in the PZ powder, in agreement with the results of Jain with  $^{119m}\text{Sn}$  in  $\text{PbZrO}_3$ . This is greatly in excess of the previously measured figure at ferroelectric Curie points, about 10% or less. The explanation of this large change in recoilless fraction is that in  $\text{PbZrO}_3$  there are lattice modes at the Brillouin-zone boundary whose frequency approaches zero at the Curie point. This softening of the lattice results in a very strong decrease in recoilless fraction.

On the other hand, the present work shows that the ferroelectric solution PTZ, also has a recoilless fraction dip which is very large, at least when one compares the material just below the Curie point and at the Curie point. It is believed that this shows that, although PTZ is a ferroelectric, it is very close to becoming an antiferroelectric, and it too has lattice modes near the Brillouin-zone boundary which become very low in frequency at temperatures near the Curie point. Confirming this conclusion, dielectric measurements have shown that it is relatively easy to drive this composition from the ferroelectric into the antiferroelectric state by the application of pressure.<sup>16</sup>

The following are the major conclusions of this study: (i) In chemically similar materials, which may become ferroelectric or antiferroelectric, the phase change makes very little difference to the nature of the bonding. (ii) The enhanced dip in Mössbauer recoilless absorption found in antiferroelectrics, provided that the free energy of the antiferroelectric phase is not too much higher than that of the ferroelectric.

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\*Present address: Aerovox Laboratories, Franklinville, N. Y.

†Present address: Austin Science Associates, Austin, Tex.

<sup>1</sup>V. G. Bhide and M. S. Multani, Phys. Rev. **139**, A1983 (1965).

<sup>2</sup>V. A. Bokov, V. P. Romanov, and V. V. Chekin, Sov. Phys. Solid State **7**, 1521 (1965).

<sup>3</sup>V. G. Chekin, V. P. Romanov, B. I. Verkin, and V. A. Bokov, Sov. Phys. JETP Letters **2**, 117 (1965).

<sup>4</sup>V. G. Bhide and H. C. Bhasin, Phys. Rev. **159**, 586 (1967).

<sup>5</sup>C. M. Yagnik, J. P. Canner, R. Gerson, and W. J. James, J. Appl. Phys. **40**, 4713 (1969).

<sup>6</sup>A. P. Jain, S. N. Shringi, and M. L. Sharma, Phys. Rev. **2**, 2756 (1970).

- <sup>7</sup>F. Jona, G. Shirane, F. Mazzi, and R. Pepinsky, *Phys. Rev.* **105**, 849 (1957).
- <sup>8</sup>V. Dvorak, *Phys. Status Solidi* **14**, K161 (1966).
- <sup>9</sup>R. Gerson, Pen-Chou Chu, and W.J. James, *J. Appl. Phys.* **38**, 55 (1967).
- <sup>10</sup>R. T. Smith, G. D. Achenbach, R. Gerson, and W. J. James, *J. Appl. Phys.* **39**, 70 (1968).
- <sup>11</sup>A. Biran, P. A. Montano, and V. Shimony, *J. Phys. Chem. Solids* (to be published).
- <sup>12</sup>J. P. Canner, Ph. D. thesis (University of Missouri-Rolla, 1969) (unpublished).
- <sup>13</sup>S. V. Karyagin, *Proc. Acad. Sci. USSR, Phys. Chem. Sec.* **148**, 110 (1964).
- <sup>14</sup>C. M. Yagnik, R. Gerson, and W. J. James, *J. Appl. Phys.* **42**, 395 (1971).
- <sup>15</sup>R. O. Bell, *J. Phys. Chem. Solids* **29**, 1 (1968).
- <sup>16</sup>D. Berlincourt, H. Krueger, and B. Jaffe, *J. Phys. Chem. Solids* **25**, 659 (1964).