

Observation of the charge order in perovskite manganite $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ by Mössbauer quadrupole effect

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Abstract The charge order in a perovskite manganite $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ was investigated by Mössbauer spectroscopy. The quadrupole splitting and the absorption line width jump to an increase when lowering the temperature below 230 K (T_{co}), which is indicative of a phase transition to a monoclinic structure due to the charge ordering, or due to a local Jahn-Teller effect due to the presence of Mn^{3+} ions. The intensity ratio of the doublet lines also changes at T_{co} . Local and dynamical Jahn-Teller effect (polarons) with a relaxation time of 10^{-8} s is present even in the metallic state.

Keywords Perovskite manganite · $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ · Charge order · ^{57}Fe Mössbauer spectroscopy · Quadrupole effect

1 Introduction

The half-doped perovskite manganite $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ has an orthorhombic structure ($Pnma$) with lattice constants $a = 5.403 \text{ \AA}$, $b = 7.612 \text{ \AA}$, $c = 5.395 \text{ \AA}$ at room temperature [1]. The material shows a metal-to-insulator (MI) transition at 230 K (T_{co}) due to the Mn^{3+} - Mn^{4+} charge and orbital ordering [2, 3]. Upon a further decrease in temperature, the material turns into a CE type antiferromagnet with $T_N = 180 \text{ K}$. Goff and Attfield [4] proposed that the charge ordered structure has a monoclinic symmetry ($P2_1/m$) with lattice constants $a = 10.8700 \text{ \AA}$, $b = 7.488923 \text{ \AA}$,

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$c = 5.3499 \text{ \AA}$, and $\beta = 90.069^\circ$ at 10 K. The structure contains three independent Mn sites, Mn1, Mn2a, and Mn2b, occupied by Mn^{4+} , Mn^{3+} , and Mn^{3+} ions respectively. The phenomenon has been intensively investigated mostly by diffraction, transport and static magnetic measurements, while measurements concerning its dynamic property and local structure have not been conducted so much. Mössbauer spectroscopy is a microscopic and dynamic probe with observation time of 10^{-8} s. Especially the quadrupole interaction is very sensitive to the local structure around the ions of interest. In this research, we have applied Mössbauer spectroscopy in order to investigate the change in local structure around Mn ions caused by the charge ordering in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$.

2 Experiments

A single crystal of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ with 0.5% ^{57}Fe substituting for Mn was prepared by the FZ method in oxygen atmosphere. The resistivity measurement confirmed that the specimen still exhibits the MI transition around 230 K. A (121) plane disk with 6.2 mm diameter and 70 μm thickness was used as absorber. The ^{57}Fe Mössbauer spectroscopy was conducted in conventional transmission geometry by using ^{57}Co -in-Rh (25 mCi) as the γ ray source. The Doppler velocity scale was calibrated with respect to Fe-metal. Lorentzian line shapes were assumed for the analysis.

3 Results and discussions

In Fig. 1, the spectra around T_{co} are shown. The spectrum consists of an asymmetric doublet with intensity ratio $I_2/I_1 = 0.90$ at 298 K. The isomer shift (IS) and quadrupole splitting (QS) at 298 K are 0.36 mm/s and 0.14 mm/s, respectively, indicating that the substituting ^{57}Fe ions are in 3+ state and correctly occupy octahedral Mn sites. Using the structure parameters [1] and assuming a point charge model for the electric potential of i -element $V^{(i)}$, the electric field gradient (EFG) tensor can be calculated by the summation over lattice, $V_{pq} = \sum_i (\partial^2 V^{(i)} / \partial p \partial q)$. Here (p, q) denote (x, y, z) . Diagonalizing the 3×3 matrix yields $QS_{\text{cal}} = 0.10$ mm/s and $(I_1/I_2)_{\text{cal}} = 0.93$ (with $\eta = 0.8$, $\theta = 73^\circ$, and $\varphi = 18^\circ$), both of which coincide well with the observations. Below 230 K, a broadening of the spectrum and an increase of the QS are seen. It is not clear whether the spectrum is composed of three subspectra corresponding to Mn1, Mn2a, and Mn2b sites, but here we analyze it to be one doublet. The spectra at 150 K, 79 K, and 4.2 K are clearly split by a magnetic hyperfine field, which is well consistent with the antiferromagnetic nature of this material. Unfortunately we cannot determine $e^2qQ/2$ in the magnetically ordered state, since we do not have information about the directions of the EFG axes. Hereafter we concentrate on the parameters in the paramagnetic region.

The IS increases almost linearly with decreasing temperature and no change is seen at 230 K. This indicates that the substituting Fe^{3+} ions remain in the 3+ state through T_{co} . The temperature dependencies of the QS and the absorption line width (W) are shown in Fig. 2. The QS is almost constant above 230 K, but jumps to an increase below 230 K. The QS value reaches 0.33 mm/s at 180 K. By using the structure parameters at 10 K [4], the QS_{cal} at Mn1, Mn2a, and Mn2b sites are

Fig. 1 Mössbauer spectra of ^{57}Fe -substituted $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ specimen around the charge order temperature

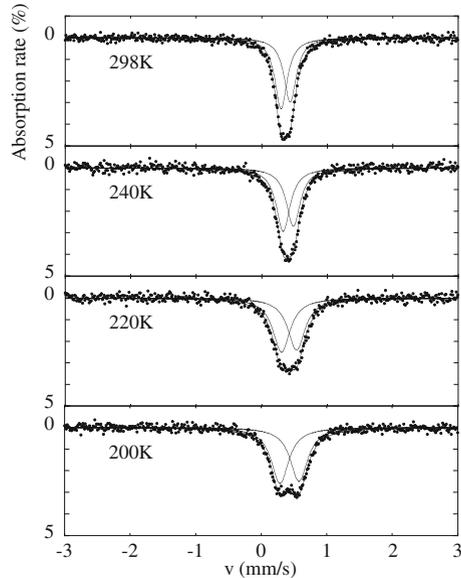
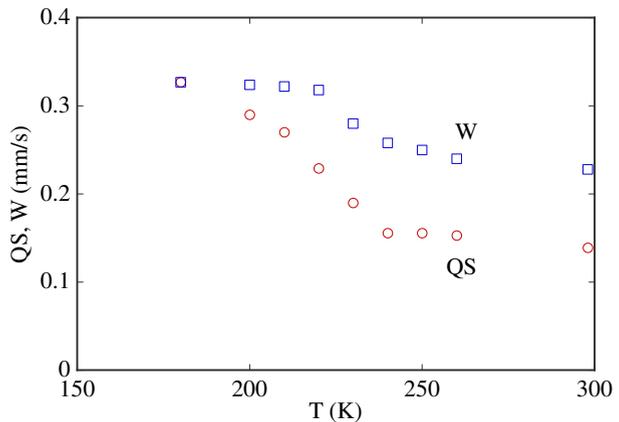


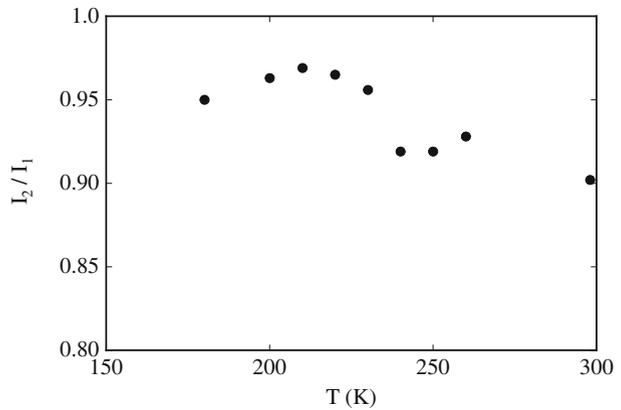
Fig. 2 Temperature dependence of the quadrupole splitting (QS) and the line width (W)



calculated to be 1.97, -0.92 and 0.89 mm/s, respectively. The observed value is not as large as expected, presumably because of the higher measurement temperature, but its increasing nature through T_{co} is just consistent. The W also shows a similar temperature variation. These observations are indicative of a phase transition to a monoclinic structure due to the charge ordering, or to a local Jahn-Teller (JT) effect due to the presence of Mn^{3+} ions. As shown in Fig. 3, the intensity ratio I_2/I_1 also changes to about 0.95 below 230 K. This suggests a change in the EFG axes, which is another plausible consequence of the charge order phase transition.

It is noted in Fig. 2 that W gradually increases with decreasing temperature even in the metallic state (above 230 K). This is abnormal in the sense of usual lattice vibrations. We assume that this is due to the local and dynamical JT effect, or polarons, with a relaxation time of about 10^{-8} s. The presence of such dynamical polarons in

Fig. 3 Temperature dependence of the intensity ratio of doublet lines (I_2/I_1)



the perovskite manganites [5] is considered to be the cause of the high resistivity ($10^{-2} \Omega\text{cm}$) in the metallic state.

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