Ultrasonic Study of Orbital and Charge Orderings in La$_{1-x}$Sr$_x$MnO$_3$ ($x = 1/8$)

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Abstract

In order to investigate orbital and charge orderings in perovskite manganite La$_{1-x}$Sr$_x$MnO$_3$ with $x = 1/8$ (Mn$^{3+}$ : Mn$^{4+}$ = 7 : 1), we have measured elastic constants by ultrasonic experiments. La$_{0.875}$Sr$_{0.125}$MnO$_3$ shows successive structural phase transitions at $T_c = 275$ K and $T_{co} = 150$ K. Above $T_c$, the elastic constant $(C_{11} - C_{12})/2$ exhibits a remarkable softening, while $C_{44}$ shows a monotonous increase with decreasing temperature. The softening of $(C_{11} - C_{12})/2$ arises from the coupling of quadrupole moment of $e_g$ orbital in Mn$^{3+}$ ion to elastic strain. Furthermore, the $(C_{11} - C_{12})/2$ and $C_{44}$ exhibit a considerable softening above $T_{co}$, which is caused by the coupling of charge fluctuation associated with the distribution of Mn$^{3+}$ : Mn$^{4+}$ = 7 : 1 to elastic strain.

Key words: quadrupole ordering, charge ordering, elastic constant

Perovskite manganite La$_{1-x}$Sr$_x$MnO$_3$ ($x = 1/8$) shows successive structural phase transitions at $T_c = 275$ K and $T_{co} = 150$ K and a ferromagnetic phase transition at $T_f = 200$ K [1]. These orderings originate in the spin, charge (Mn$^{3+}$, Mn$^{4+}$) and orbital ($d(3z^2 - r^2)$, $d(x^2 - y^2)$) degrees of freedom in La$_{0.875}$Sr$_{0.125}$MnO$_3$. The structural phase transition at $T_c$ is accompanied by the Jahn-Teller distortion from pseudo cubic to pseudo tetragonal due to the $e_g$ orbital in Mn$^{3+}$ ion. While the structural phase transition at $T_{co}$ changes the perovskite structure, which is warped to pseudo tetragonal, to pseudo cubic. It has been pointed out that the structural phase transition at $T_{co}$ is charge ordering characterized by the coexistence ratio Mn$^{3+}$ : Mn$^{4+}$ = 7 : 1 [2]. We paid attention to the coupling of $e_g$ orbital or charge fluctuation of Mn ions to lattice in La$_{0.875}$Sr$_{0.125}$MnO$_3$ and measured the elastic constants by ultrasonic experiments.

Fig. 1 shows the temperature dependence of the elastic constants in La$_{0.875}$Sr$_{0.125}$MnO$_3$. Above $T_c$, the $(C_{11} - C_{12})/2$ shows a remarkable softening, while the $C_{44}$ exhibits a monotonous increase in lowering temperature. These observations are similar to those of La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.12, 0.165$) and explained by the quadrupolar susceptibility of a 3d electron in $e_g$ orbital doublet[3]. The temperature dependence of the elastic constant $C_{T3} = (C_{11} - C_{12})/2$ is described by

$$C_{T3}(T) = C_{T3}^0 - N g_{T3}^2 \frac{\chi_{T3}(T)}{1 - g_{T3}^2 \chi_{T3}(T)}.$$  (1)

Here $\chi_{T3}$ is the quadrupolar susceptibility for $O_e^2$ or $O_{d2}^2$ of a 3d electron in $e_g$ orbital doublet, $C_{T3}^0$ is a background and $N$ is the number of Mn$^{3+}$ ions in unit volume. The $g_{T3}$ is a coupling constant of quadrupole-strain interaction as $H_{QQ} = - \sum_n g_{T3}(O_e^2(t)\xi_n + O_{d2}^2(t)\xi_3)$. The $O_e^2$ and $O_{d2}^2$ are
quadrupolar operators on 3d electron and $e_{\alpha}$ and $e_{\alpha}'$ are elastic strains with $\Gamma_3$ symmetry. The $g_{\alpha\alpha}'$ is a coupling constant for the inter-site quadrupolar interaction as $H_{QQ} = -\sum g_{\alpha\alpha}' ([O^z_{\alpha} O^z_{\alpha}'(i)] + [O^z_{\alpha} O^z_{\alpha}'(i)])$. The solid line on the $(C_{11} - C_{12})/2$ above $T_c$ in Fig.1 is the calculated curve with Eq. (1) and we obtained $|g_{\alpha\alpha}'| = 462$ K and $g_{\alpha\alpha}' = 20$ K. These coupling constants are comparable with those of $La_{1-x}Sr_xMnO_3$ ($x = 0.12, 0.165$) [3].

The other important finding is that both of $(C_{11} - C_{12})/2$ and $C_{44}$ show a softening above $T_c$ definitely. These softenings appear around $x = 1/8$, for instance $La_{0.88}Sr_{0.12}MnO_3$ [3]. The quadrupolar susceptibility of an electron in $e_{\alpha}$ orbital doublet could not lead to the softening of $C_{44}$ above $T_c$. Therefore, the softening of $C_{44}$ above $T_c$ originates from the coupling of charge fluctuation of Mn ions associated with the coexistence ratio of $Mn^{4+} : Mn^{5+} = 7 : 1$ to elastic strain with $\Gamma_3$ symmetry such as $H_{CS} = -\delta Q_{T\Sigma}$. Here $Q_{T\Sigma}$ is the order parameter of the charge ordering. The softening of $(C_{11} - C_{12})/2$ probably arises from the anharmonic coupling of elastic strain with $\Gamma_3$ symmetry to the order parameter fluctuation. In the case of charge ordering such as Ybf$_{3}A_{N}O_3$ [4], the softening of the elastic constant owing to the charge fluctuation of Ybf$^{2+}$ and Ybf$^{3+}$ ions is written as $C_{ij}(T) = C_{ij}^0(T - \theta_{T\Sigma})^2/(T - \theta)$. The equation can be applied to the softening of $C_{44}$ above $T_c$ in the present case. The solid line on the $C_{44}$ above $T_c$ in Fig. 1 is the calculated curve with this equation and we obtained the characteristic temperatures $\theta_{T\Sigma} = 20$ K and $\theta = 137$ K of $C_{44}$.

Colossal magnetoresistance around $T_c$ is also observed in $La_{0.87}Sr_{0.12}MnO_3$ [5]. Therefore, we have measured the elastic constants in $La_{0.87}Sr_{0.12}MnO_3$ under several magnetic fields. Fig. 2 shows the temperature dependence of the elastic constants $(C_{11} - C_{12})/2$ and $C_{44}$ around $T_{co}$ in $La_{0.87}Sr_{0.12}MnO_3$ under several magnetic fields along [110] and [100], respectively. The $C_{44}$ remains to show a pronounced softening about $10\%$ under 12 T. This means the charge fluctuation of Mn ions characterized by $Q_{T\Sigma}$ is still relevant even in fields up to 12 T. In contrast, the softening of $(C_{11} - C_{12})/2$ above $T_{co}$ becomes small gradually with increasing magnetic field. The charge ordering point corresponding to the minimum of $C_{44}$ moves to high temperatures with increasing magnetic field rapidly. The charge ordering of Mn ions in $La_{0.87}Sr_{0.12}MnO_3$ becomes stable under magnetic fields.

References