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SANS Study on $Pr_{0.7}Ca_{0.3}MnO_3$ System as 'Magnetic Relaxor'

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We report SANS study on $Pr_{0.7}Ca_{0.3}MnO_3$. It is shown that, in low-Q region, the intensity has Q^{-4}-dependence, which indicate that there exist ferromagnetic clusters with mesoscopic size. Upon application of magnetic field, the intensity decreases substantially in spite of that the total magnetization increases. This is consistently interpreted that the size of microcluster has increased upon application of magnetic field. the results are discussed phenomenologically within the framework of TDGL theory, which suggests that in ZFC condition, the system tends to stay on in a metastable state of 'two-phase coexistence'. The close relationship with the dielectric behavior in relaxor ferroelectrics is pointed out.

KEYWORDS: collossal magnetoresistance, magnetic small angle scattering, two-phase coexistence

§1. Introduction

The CMR effect exhibited by various perovskite-based Manganese Oxides has been subjected to extensive studies from both experimental and theoretical aspects. Basically it is understood that the CMR effect takes place at the critical region where the double exchange mechanism to stabilize ferromagnetic state and the superexchange mechanism to stabilize antiferromagnetic state compete with each other in the substance.

From the experimental observations, on the other hand, it has become clearer that at low temperatures, the CMR substances are not in a uniform thermodynamically stable phase, but tend to be in a heterogeneous state where the two competitive phases with mesoscopic size are coexisting as a thermodynamically metastable state.[1–3)]

Small angle neutron scattering is a powerful technique to elucidate the mesoscopic magnetic 'structure' in a system within a length scale of 1∼100 nm. In particular, if there are mesoscopic ferromagnetic domains with smooth surface embedded on non-magnetic medium as postulated in the above model, they should give rise to SANS spectrum obeying so-called Porod rule.

The purpose of the present study is to carry out SANS experiments on several CMR substances in order to elucidate the properties of magnetic 'structure' in mesoscopic length scale. The results are then discussed phenomenologically within the framework of TDGL (time-dependent Ginzburg-Landau) theory. In particular, close relationship with the physical properties of relaxor ferroelectrics is pointed out.

§2. Experimental

SANS experiments on a few CMR substances have been carried out at SANS-J spectrometer installed at JRR-3M reactor, Japan Atomic Energy Research Institute. In this paper, we only describe the results on $Pr_{0.7}Ca_{0.3}MnO_3$ in order to focus our attention to the most typical material which has been extensively discussed.[4–8)]

Single crystals of $Pr_{0.7}Ca_{0.3}MnO_3$ with size of 11.8 mm×5 mm ϕ were grown at Moritomo Laboratory, Nagoya University. A sample was mounted on the goniometer with the b-axis (in *Pnma* setting) vertical. The temperature of the specimen was controlled within ±0.05 K. The magnetic field of the maximum value of H=1 T was applied in horizontal geometry. A two-dimensional detector was set at 1.5 m and 10 m flight path between the sample and the detector.

The observed intensity distribution on the 2-D counter showed definite anisotropy elongated along the b-axis. Since we are mainly interested in radial distribution, we present the results after taking azimuthal average in Fig. 1. It is noticed that the spectra commonly divided into two regimes : 'high-Q' regime and 'low-Q' regime. In 'high-Q' regime, the Q-dependence is of Lorenzian type, indicating the intensity is due to spin fluctuations. In 'low-Q' regime the intensity has Q^{-4}-dependence obeying Porod's rule, which indicates that there exist ferromagnetic clusters with mesoscopic size. It is also noticed that in H=0 case at the low temperatures the intensity starts to bend over to exhibit a 'shoulder' as Q-value is further decreased. From Fig.1(b), we see that most remarkable change in $I(Q)$ upon application of the magnetic field takes place in the 'low-Q' regime at lower temperatures : while the Q-dependence itself obeys the same Q^{-4}-law, the intensity is decreased by a factor of 10^{-2}. At the same time, the 'shoulder' disappeared from the observed Q-range.

These experimental results have been analyzed assuming that the overall spectra are expressed by the sum of scattering due to the ferromagnetic cluster and the scattering due to spin fluctuations where the size of the

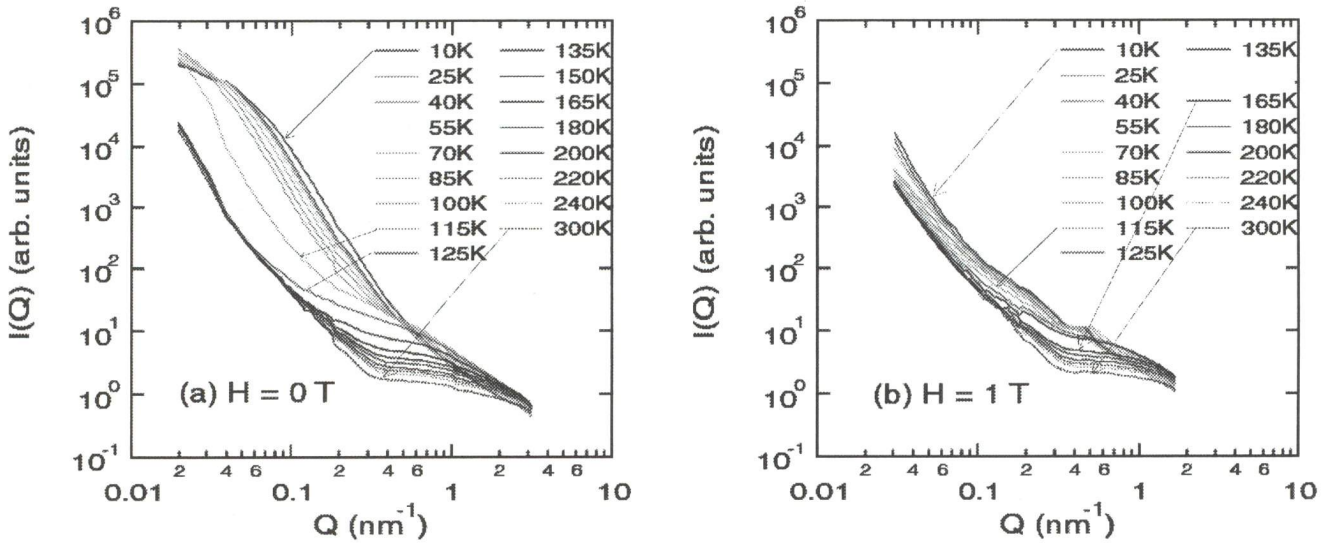

Fig. 1. Temperature variation of the SANS spectra $I(Q)$ after averaging in the azimuthal direction at (a) $H = 0$ T and (b) $H = 1$ T.

cluster and the correlation length of the fluctuation are the disposable parameters to be fixed by the least square fitting procedure.

The results of the analysis of the spectra, in particular of the low-Q regime are summarized as follows : Under ZFC (zero field cooling) condition, the system at low temperatures is in the state of 'two-phase' coexistence where FM (ferromagnetic metallic) micro cluster with the average radius of $R \sim 40$ nm are embedded randomly on AFI (antiferromagnetic insulator) background. Upon application of magnetic field of 1 T, the ferromagnetic clusters start to coalesce to form macroscopic domains with the size of order 3 μm without changing the total volume of FM region appreciably.

§3. Heterophase Fluctuation and Stability of 2-phase Coexistent State

We define two primary order parameters associated with the charge/orbital ordering process. The one is the Ising variable, ψ, specifying the $3d$ orbital state on Mn^{3+} site. The other is the amplitude of local J-T active mode, Q_i, around the Mn^{3+} site.

The long range ordered state in $Pr_{0.7}Ca_{0.3}MnO_3$ is characterized by the condensation of the following ORW (orbital wave) and LDW (lattice distortion wave) :

$$\begin{aligned} &\text{ORW}: \quad \psi(\boldsymbol{r}) = \hat{\psi}\exp(i\boldsymbol{k}_0\cdot\boldsymbol{r}), \\ &\text{LDW}: \quad Q(\boldsymbol{r}) = \hat{Q}\exp(i\boldsymbol{k}_0\cdot\boldsymbol{r} + i\pi/2), \\ &\qquad\quad \boldsymbol{k}_0 = [1/2, 0, 0]_{\text{ortho}} \end{aligned} \tag{3.1}$$

In addition, we also take into account the uniform contraction of the lattice in the $[100]_{\text{ortho}}$-direction, e, which takes place upon transition.

$$e(\boldsymbol{r}) = \hat{e}\exp(i\boldsymbol{k}_0\cdot\boldsymbol{r})_0 \tag{3.2}$$

In order to discuss the effect of fluctuations of the order parameters in the vicinity of the ground state, we assume that the amplitudes $\hat{\psi}, \hat{Q}$ and $\hat{e}$ are slowly varying in the space. Thus, $\hat{\psi}(\boldsymbol{r}), \hat{Q}(\boldsymbol{r})$ and $\hat{e}(\boldsymbol{r})$ are considered to be semimacroscopic thermodynamical variables which should be handled within the framework of Ginzburg-Landau type phenomenological treatment.

We start with establishing the free energy density associated with the orbital ordering as follows :

$$f = f_{\text{orb}}(\hat{\psi}) + f_{\text{ph}}(\hat{Q}, \hat{e}) + f_c(\hat{\psi}, \hat{Q}, \hat{e}) \tag{3.3}$$

$$f_{\text{orb}}(\hat{\psi}) = \frac{\tau}{2}\hat{\psi}^2 + b\hat{\psi}^4 + c\hat{\psi}^6 + \kappa(\nabla\hat{\psi})^2, \tag{3.4}$$

$$f_{\text{ph}}(\hat{Q}, \hat{e}) = \frac{\omega_0^2}{2}\hat{Q}^2 + \frac{1}{2}c_{11}\hat{e}_1^2 + \frac{1}{2}c'\hat{e}_2^2, \tag{3.5}$$

$$f_c(\hat{\psi}, \hat{Q}, \hat{e}) = g\hat{\psi}\hat{e}_2 + g'\hat{\psi}^2\hat{e}, \tag{3.6}$$

Where $\tau \propto T - T_c, b < 0, c > 0, \kappa > 0$. In eq.(3.5) ω_0 is the frequency of the TA zone boundary phonon ; c_{11} and c' are the elastic constants for dilatational and deviatoric strains. Eq.(3.6) describes electron-phonon couplings in the system. The first term gives the local Jahn-Teller coupling and the second term gives the effect of the contraction of the lattice which takes place irrespective of the value of $\psi(= \pm 1)$.

Formally, we could find the stable state by solving the Euler equations associated with $\hat{\psi}(\boldsymbol{r}), \hat{Q}(\boldsymbol{r})$ and $\hat{e}(\boldsymbol{r})$. However, since the energy is highly non-linear, it is practically impossible to find analytic solutions. Therefore, we proceed as follows : We set up the TDGL equations of the system and starting from a suitable initial state, we follow the time development of the order parameters by computer simulation until the system stops time variation to stay on in a (meta)stable state. In the simulation process of time development we effectively make use of the adiabatic approximation assuming that the electronic state of e_g-electron is instantaneously following the Jahn-Teller distortion of the surrounding oxygens.

(i)g'=0

The result of $\hat{\psi}(\boldsymbol{r})$-pattern when the coupling to bulk strain is neglected is given in Fig.2(a). The system is characterized by a regular array of two variants of the ordered states. The periodicity of the 'stripe's is of

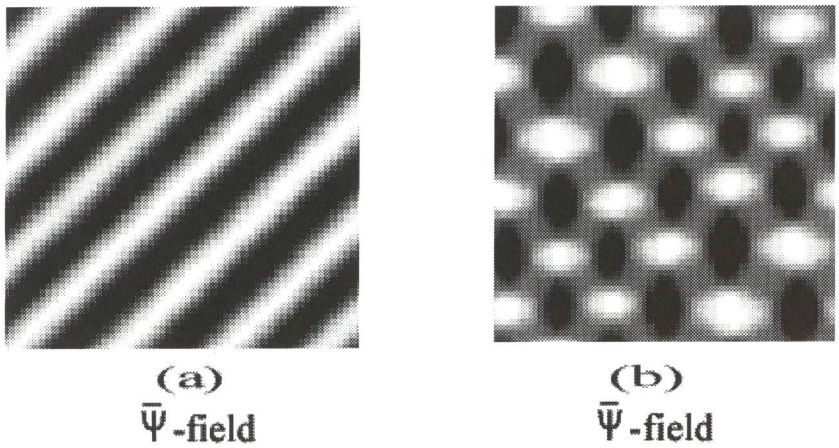

Fig. 2. (a) $\hat{\psi}(\boldsymbol{r})$ pattern when $g' = 0$ (no coupling to the bulk contraction. Black and white regions correspond to the two variants of the ordered state.) (b) $\hat{\psi}(\boldsymbol{r})$ pattern when $g' \neq 0$ (coupling to the bulk contraction is included). The system is composed of three microregions: two variants of the ordered state plus the disordered state ($\hat{\psi} = 0$) represented by the 'gray' region.

mesoscopic size. In this connection, it should be remarked that a number of materials generally expressed by $A_{0.5}B_{0.5}MnO_3$ (A:La, Pr, Y, Nb,..., B:Sr, Ca) stabilize an incommensurate orbital order with incommensurability $\delta \sim 0.1a*_{\text{ortho}}$. We may be able to identify the 'stripe' to be the discommensuration pattern realized in these incommensurate structures.

(ii)$g' \neq 0$

The results of similar patterns when the coupling to bulk strain is included is given in Fig.2(b). In contrast to the pattern of Fig.2(a), the whole system is divided into three microdomains : two variants of the 'ordered phase' and the 'disordered phase'. That is, the system seems to stay on in the metastable state of two phase coexistence. The size of the microdomain is of same order as the width of the 'stripe'.

§4. Discussions

In the preceding section we have demonstrated that when the strong coupling to bulk strain exists, the electron-phonon system tends to stay on in the metastable state of the 'two phase coexistence' where the microdomains of ordered phase is coherently embedded in the disordered phase.

Since the free energy density expression in eq.(3.4) is quite general, we may be able to apply the same argument to other physical systems. One of such system is the β-based martensite alloys. In fact, Onuki[9,10] first pointed out the importance of the coupling of odd orders (typically $e^2\psi$-term) to realize the metastable two-phase coexistent state at martensite transformations.

Another important candidate of such system is the relaxor ferroelectrics. It is known that the relaxors are in the state of two-phase coexistence (ferroelectric and paraelectric) in a wide temperature range where the dielectric constant shows anomalously large value. Recently, Tokura[11] pointed out the similarity of CMR substances to relaxors.

The essential origin of the similarity between CMR substances and relaxors would reside in that both systems shares the same phenomenological free energy density eq.(3.4) if we interchange the orbital order parameter ψ and polarization P.

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1) S.Mori, T.Katsufuji, N.Yamamoto, C.H.Chen and S-W.Cheong: Phys. Rev. B**59** (1999) 13573.
2) N.Fukumoto, S.Mori, N.Yamamoto, Y.Moritomo, T.Katsufuji, C.H.Chen and S-W.Choeng: Phys. Rev. **60** (1999) 12963.
3) M.Uehara, S.Mori, C.H.Chen and S-W.Cheong: Nature **399** (1999) 560.
4) Y.Tomioka, A.Asamitsu, Y.Moritomo, H.Kuwahara and Y.Tokura: Phys. Rev. Lett. **74** (1995) 5108.
5) Z.Jirak, S.Krupicka, V.Nekuasil, E.Pollart, G.Willeneuve and F.Zounova: J. Magn. Magn. Mater. **15-18** (1980) 519.
6) H.Yoshizawa, H.Kawano, Y.Tomioka and Y.Tokura: Phys. Rev. B**52** (1998) 13145.
7) V.Kiryukhin, D.Casa, J.P.Hill, B.Keimer, A.Vigliante, Y.Tomioka and Y.Tokura: Nature (London)**386** (1997) 813.
8) D.E.Cox, P.G.Radaelli, M.Marezio and S-W.Choeng: Phys. Rev. B**57** (1998) 3305.
9) A.Onuki: J. Phys. Soc. Jpn, **68** (1999) 5.
10) A.Onuki: *Proc. Int. Conf. Solid State Phase Trans.* (JIMIC-3) (1999) 533.
11) T.Kimura, Y.Tomioka, R.Kumai, Y.Okimoto and Y.Tokura: Phys. Rev. Lett. **83** (1999) 3940.