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Colossal Response Induced by Hetero-Structure Fluctuation

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Some materials exhibit a huge response to an applied field, as a result of mesoscopic hetero-phase fluctuation. The most typical example is dielectric relaxors where the formation and development of polar nano-cluster play an important role in their characteristic dielectric responses. The phenomenon is ubiquitous and is found in variety of materials such as martensitic alloys, colossal magneto-resistance materials and ferroelastics. The response characteristics may be termed "super-susceptibility", which cannot be described by the linear response theory based upon atomic fluctuations. This paper picks up three examples of materials, and points out that common features of the phenomenon. The computer simulation using the time-dependent Ginzburg-Landau equation of the dielectric response in relaxors is presented.

Key words: Hetero-structure, ferroelectrics, relaxor, dielectric response, super-susceptibility, Ginzburg-Landau equation

1. INTRODUCTION

The macroscopic structure of material is not merely determined by microscopic atomic arrangement but sometimes consists of intermediate mesoscopic structures super-structure) which gather to form an overall structural hierarchy. Typical examples are super-molecules in biomaterials, lamelli in polymers, domain structures in ferroelectrics and ferromagnetics.

A response to an external field is expressed by a susceptibility, which is the most important material constant characterizing a macroscopic physico-chemical property of materials. The susceptibility has so far been related to fluctuation of microscopic physical quantities by the linear response theory. However, when materials possess the structural hierarchy, the framework is not entirely effective and the new concept could be much more useful which relates the response to fluctuations of physical quantities characterizing mesocopic structures. For example, the shape-memory effect of martensitic alloys can be explained not by the well-established microscopic elastic-response theory but by the fluctuations of macroscopic twin structure. Such examples have been recently found in variety of materials; the huge dielectric response in relaxors and colossal magnetic response in some oxides magnetics etc. Based upon the idea, the paper presents some examples of the colossal response termed super-susceptibility originated from mesoscopic structure fluctuations, and the result of simulations using the time-dependent Ginzburg-Landau (TDGL) theory.

2. SUPER-SUSCEPTIBILITY INDUCED BY SUPER-STRUCTURE

2.1 Colossal elastic response of ferroelastics

Here is shown an example where the displacement of domain boundary induces quite large elastic response in ferroelastic $Pb_3(PO_4)_3$ (LP)[1]. LP exhibits a ferroelastic phase transition at 180C from trigonal R3m to monoclinic C2/m[2]. In the monoclinic phase, there exist three types of domains (S_1,S_2,S_3) which are related to each other by the 3-fold axis in the trigonal phase and separated by two kinds of boundaries determined by minimizing the elastic energy at the boundaries[3]. One is the crystallographic mirror plane specified by the rational Miller indices (termed W), and another the boundary specified by irrational indices. A single crystal has a cleavage perpendicular to the 3-fold axis. A thin cleavage plate which sometimes exhibits two-type of domains (S_1, S_2) separated by the W-type boundary as shown in Fig.1(a). The application of shear stress parallel to the boundary induces the state where S_1 is preferential (Fig.1(b)). However the perfect mono-domain state cannot be realized and the fine S_2 state always remains even under large shears. Release of shear restores the sample to the original state (a). Then the application of shear stress along the opposite direction induces the S_2-preferential state as shown in Fig.1(c). It should be noticed that the plate shape is transformed large through the shift of domain boundary under the shear stress. It transforms as if it is a rubber. The measured stress-strain curve is shown in Fig.2. The strain shows a nonlinear increase with shear stress and is saturated. The elastic constant determined by this experiment is 1.5×10^7 Pa, which is three-order of magnitude smaller than that determined by the Brillouin scattering using a mono-domain specimen. The value is even much smaller than that of polyethylene.

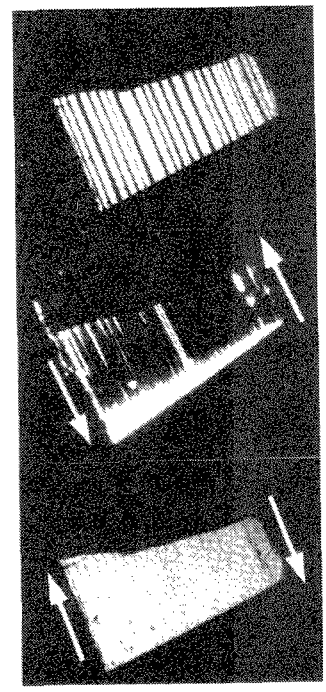


Fig.1 Change of domain structure of $Pb_3(PO_4)_3$. under the pure stress along the edge of W-type domain boundary. (see the text)

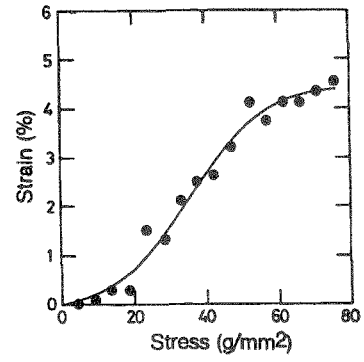


Fig.2 Strain-stress curve observed in $Pb_3(PO_4)_3$

2.2 Huge dielectric response of relaxors

Relaxors[4] ABO_3 where the A-site is occupied by Pb and the B-site by two kinds of

metal ion with different valency exhibit huge dielectric constant The dielectric response of relaxors is characterized by the frequency dispersion: The peak temperature increases and the peak value of the real part of dielectric constant decreases with increase of frequency as shown in Fig.3(a). In particular, the prototype relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) has no phase transition, although the dielectric constant exhibits a large and broad maximum: The average structure remains to be cubic Pm3m down to the liquid He temperature with the local break of the inversion symmetry. However, the long-range order can be induced by the application of the electric field. This strongly depends on the pre-history of specimens as shown in Fig 3(b)[5],[6]: Temperature dependence of birefringence Δn shows quite different paths, depending on zero-field cooling (ZFC), field heating(FH) after ZFC, field cooling(FC) and FH after FC. In particular, the behavior of the FH after ZFC varies with the heating velocity of the specimen, which suggests the process is meta-stable. Thus the time change of Δn under the electric field was measured and the result is shown in Fig.3(c). The remarkable effect was observed: Δn, equivalent to the square-root of the long-range order, has a quite long incubation time τ which sometimes reaches several ten hours and develops abruptly after τ. With decreasing temperature, τ increases and at the low temperature region, it exceeds the laboratory time

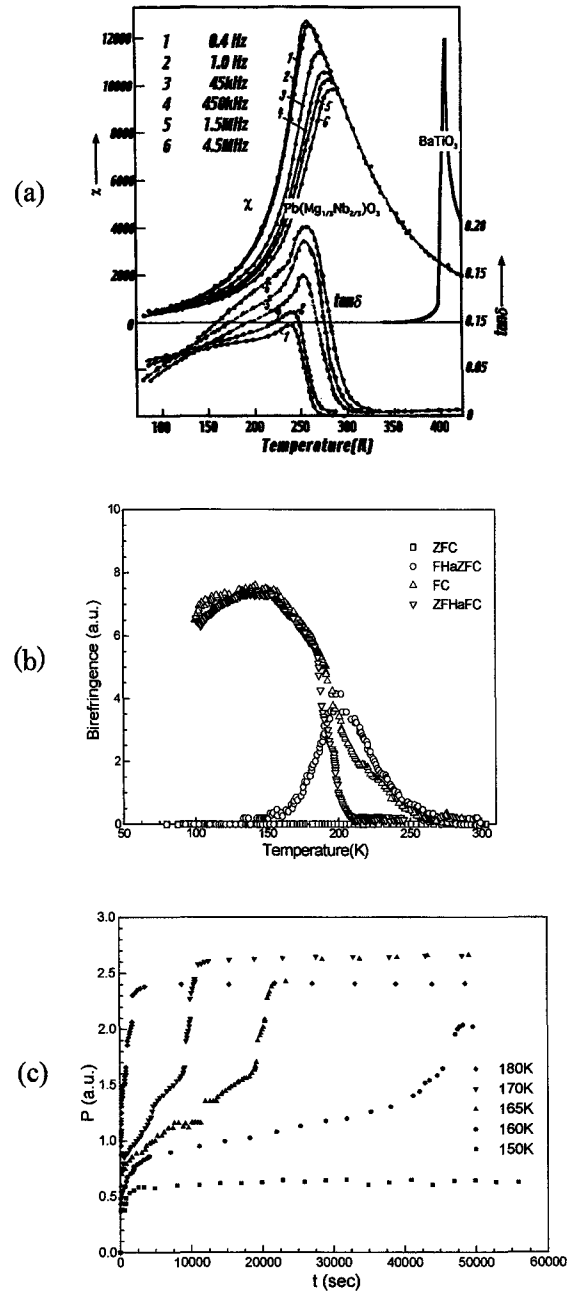


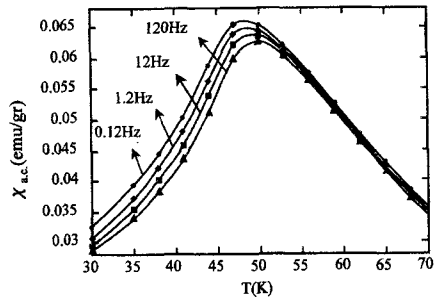
Fig.3. Frequency dependence of dielectric constant(a), pre-histry dependence of the field-induced Δn(b), and time-development of Δn under the electric field(c) of $Pb(Mg_{1/3}Nb_{2/3})O_3$

. Epoch-making experiments were performed by Burns et al[8], who measures precisely the temperature dependence of the refractive index of PMN and found that it deviates from the high-temperature linear dependence at the temperature 300C higher than the dielectric maximum temperature. They concluded that it comes from the nucleation and growth of the polar

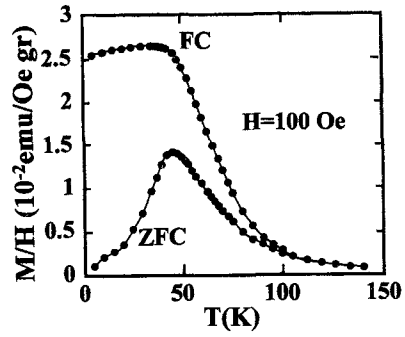
nano-regions in the cubic matrix. Thus the coexistence of two phases and its freezing down to the low temperature is a characteristic of relaxors, which, together with the dielectric behaviors shown in Figs. 3(a), 4(a) and 5(a), should be criterions for the applicability of theories of relaxors.

2.3 Colossal magnetic response of magnetic oxides

Similar phenomena have been observed in perovskite Mn oxides which shows colossal magnetic resistance (CMR)[7]-[9]: The application of magnetic field induces huge change of the electric conductivity. Frequency and temperature dependences of magnetization (Fig.4(a)), pre-history dependence of the magnetization (Fig.4(b)), time change of the conductivity under the constant magnetic field (Fig.4(c)) are quite similar to the relaxor PMN in all aspect. Due to this kind of similarity, they are termed magnetic relaxors. In the CMR materials, the two-phase coexistence of ferromagnetic-metallic nano-clusters in anti-ferromagnetic-insulator with the charge-orbital ordering brings about the peculiarity. When the magnetic field is applied, the metallic nano-clusters grow and are coalesced to form percolation, which yields the bulk conductivity. This is just the same process observed in relaxors, where ferroelectric nano-cluster plays important role.



(a)



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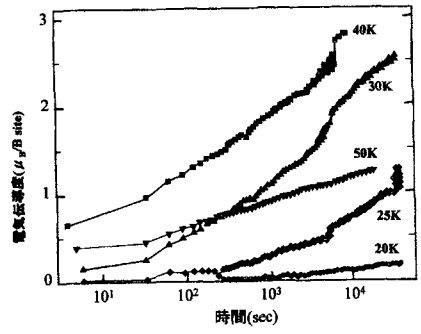

(c)

Fig.4. Frequency dependence of magnetic susceptibility(a), pre-histry dependence of M/H(b), and time-development of conductivity (c) of CMR perovskite manganate.

3. Computer simulations using the time-dependent Ginzburg-Landau theory

Peculiar responses of ferroelectric and magnetic relaxors could be summalized as follows; (1) characteristic frequency dependence of the susceptibility, (2)remarkable pre-history dependence of the order parameter, and (3)long incubation time under the external field and acceleration of the development of the order parameter after the incubation time. These features can be qualitatively explained by the

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time-dependent Ginzburg-Landau (TGDL) equation. Here, as an example, we show the simulation result on the acceleration of the long range order. Such a phenomenon has been observed in $BaTiO_3$[10]: Ferroelectric phase induced by the electric field in just above the phase transition at 120C is recovered to paraelectric phase with rather long incubation time of msec. Chandra[11] pointed out the importance of the long-range interaction of the strain field and calculated the nucleation rate and growth velocity using the Fokker-Planck equation based upon the free energy containing dielectric, elastic and their coupling terms. We performed the two-dimensional simulation with the TDGL equation using her free energy, and obtained substantially similar results. The free energy F is expressed with polarization P, strain s as follows.

$$F = V_0 \sum_i \left\{ F(P_i, s_i) + \frac{1}{2} K (s_i - < s >)^2 \right\} \quad (1)$$

where <s> is the average of strains, therefore the second term indicates the long-range interaction of strains, and

$$F(P_i, s_i) = \frac{1}{2} a (T - T_0) P_i^2 + \frac{1}{2} b P_i^4 + \frac{1}{6} c P_i^6 - E P_i + \frac{3}{2} c_E s_i^2 - q s_i P_i^2 \quad (2)$$

Using the normalized order parameter $\phi_I = P_i/P_0$ with $P_0^2 = -[b - (2q^2/c_E)]/c$, the regrouped F is expressed as

$$F = -\frac{1}{2}(a - \gamma)\phi^2 + \frac{a}{4}\phi^4 - e(1 + \frac{\gamma}{e} < \phi >)\phi + \frac{\kappa}{2} |V\phi|^2 \quad (3)$$

where

$$\gamma = \left(\frac{1}{cP_0^2}\right)\left(\frac{2Kq^2}{3c_E(3c_E + K)}\right) \quad (4)$$

and <φ> is the average order parameter e is the normalized electric field E.

The time-development of φ is expressed by the following equation.

$$\frac{\partial \phi}{\partial t} = -L\left(\frac{\partial F}{\partial t}\right) + \zeta \quad (5)$$

Here ζ correspond to a random force due to thermal excitation, and is given by

$$\langle \zeta(r,t) \rangle = 0$$
$$\langle \zeta(r,t)\zeta(r',t') \rangle = 2k_B T L \delta(r - r')\delta(t - t') \quad (6)$$

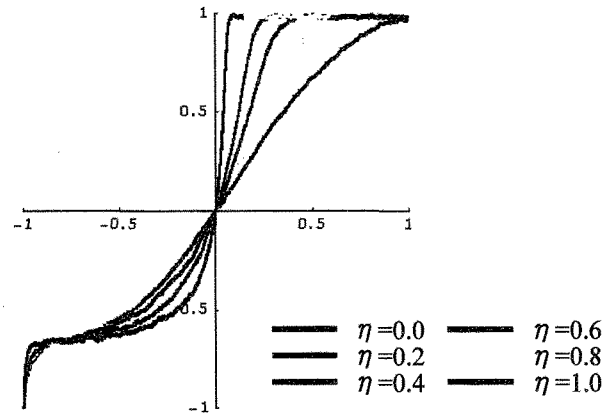
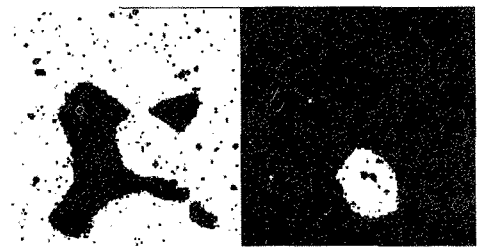


Fig.5 Simulation of the time-development of order parameter under the electric field.



(a) (b)

Fig.6 Snap-shot of two-dimensional patterns of the order parameter under the electric field. (a)the case of no long-range coupling(η=0), (b)the case of the full coupling(η=1). White parts indicate the region already inverted under the electric field.

Time dependence of φ calculated by Eq.(5) is

shown in Fig.6, where the time is normalized by the acceleration time τ_c. The acceleration becomes steep as the parameter $\eta(=\gamma/e)$ increases and the development of ϕ deviates from the conventional Avrami theory[12]. Two-dimensional distributions of ϕ are shown for two extreme cases for $\eta=0$ and $\eta=1$ in Fig7(a) and (b), respectively. At a certain time before τ_c, ϕ has already prevails on the surface in the case(a), but it still keeps local nature in the case(b). This behavior well reproduces the experimental result shown in Fig.5(a). According to Chandra, τ_c is given by

$$(\tau_c)^{-1} = \left\{\frac{\pi(\ln 2)}{3}\right\}(I_0)^{\{t/(1-\eta)^2\}} \quad (7)$$

where

$$I_0 = \exp(-E/k_BT)$$

τ_c depends strongly upon η which includes a electrostrictive constant q. If q increases 10% of $BaTiO_3$, τ_c increases by 6th order of magnitude. As the electrostrictive effect of relaxors is quite large, this explains well the huge incubation time ($>10^3$s) observed in relaxors in comparison with that (10^{-3}s) of $BaTiO_3$,

3. SUMMARY

When hetero-structures exist in materials, the movement of the boundary sometimes produces a huge response to the external field. This phenomenon is ubiquitous and is found in various materials including relaxors, ferroelastics, martensitic alloys and CMR magnetics. The most suitable approach to this problem is the time-dependent Ginzburg-Landau equation, and some intrinsic features can be explained well by the equation. It has been pointed out that the random field produces the nano-cluster in some materials, but we would emphasize that the long-range interaction of strain field also plays an important role for these peculiar phenomena.

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