Solid State Communications 240 (2016) 10–14

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Finite block pseudo-spin approach of proton glass

Kwang-Sei Lee [a], Je Huan Koo [b], Cheol Eui Lee [c,*]

[a] Department of Nano Science & Engineering, Center for Nano Manufacturing, Inje University, Gimhae 621-749, Republic of Korea
[b] Department of Electrical and Biological Physics, Kwangwoon University, Seoul 139-701, Republic of Korea
[c] Department of Physics, Korea University, Seoul 136-713, Republic of Korea

ARTICLE INFO

Article history:
Received 10 September 2015
Received in revised form
19 January 2016
Accepted 18 April 2016
by A. Pinczuk
Available online 23 April 2016

Keywords:
D. Dielectric properties
D. Ferroelectricity
D. Phase transitions

ABSTRACT

We herein propose an alternative phenomenology to explain the phase of proton glass by reference to finite block spin theory in magnetism, in which the phase may be considered as being a short-range ferroelectric ordering of block pseudo-spins comprised of random pseudo-spins that have a majority of individual pseudo-spins in a given sense. By making use of the Curie law of block pseudo-spins, we obtained the dielectric susceptibility for the lower and higher temperature approximations of the *Brillouin function*. The experimental results for the susceptibility in hydrogen-bonded mixed crystals of ferroelectric $RbH_2P(As)O_4$ and antiferroelectric $NH_4H_2P(As)O_4$ were thus fitted fairly well at low temperatures in the proton glass phase whereas some deviation from our formulation was seen at high temperatures in the paraelectric phase.

1. Introduction

None of the early known pyroelectric materials were ferroelectric in the sense of long-range ordering for reorientational electric dipole moments until 1920 when Valasek [1] discovered the spontaneous polarization in the crystal of sodium potassium tartrate tetrahydrate ($NaKC_4H_4O_6 \cdot 4H_2O$) better known as Rochelle salt. Since the discovery of KH_2PO_4 (KDP) with a ferroelectric transition at 122 K and $NH_4H_2PO_4$ (ADP) with an antiferroelectric transition at 148 K [2,3], the XH_2YO_4 (X=K, Rb, Cs, NH_4, Tl; Y=P, As) family has been one of the most extensively studied hydrogen-bonded ferroelectric crystals [4–10]. The Ising-type pseudo-spin formalism of the proton configurations in double potential wells for the XH_2YO_4 family crystals was well developed [4,5]. The proton tunneling model [4,11,12] was also suggested with a focus on quantum tunneling of protons between two potential wells. Phenomenological analysis based on the Landau–Ginzburg theory of structural phase transitions [4], where gradient and surface terms are taken into account, was successfully applied for various multiferroic and nanoferroic phenomena irrespective of the different microscopic theories [13,14]. The renormalization group theoretical treatment [15] of critical fluctuations in the ferroelectric materials was also developed. Even though electron–phonon interaction (EPI) effects are considered as a driving mechanism of ferroelectricity from the strong support from the isotope shift of T_c [16], a systematic and microscopic approach on EPI is still necessary.

Ever since the 1970s, spin glass has been the focus of considerable attention as a research topic in the physics of condensed matter [17–19] . An early approach by Edwards and Anderson [20] made use of a theory that focused on short-range interactions, in which a proper order parameter was defined as being the mean of the squares of the averages of the local spin operators that have nonzero values below a finite temperature. This work was later extended by using the Sherrington-Kirkpatrick (SK) model [21], which yielded the corresponding long-range interactions by using a mean field approximation.

The first types of spin glass systems consisted of dilute solutions of magnetic transition metal impurities within the noble metal hosts. The atomic moments of the impurities induce a magnetic polarization of the conduction electrons in the surrounding host metal. The polarization is positive in some locations and negative in others. The impurity moments are then susceptible to the local magnetic field produced by the polarized conduction electrons, which tend to align themselves along the randomly distributed local fields. Other systems of spin glasses have also been found in magnetic insulators and amorphous alloys, in which dependence on the distance of the interaction between the local moments is in random competition, and is entirely different in nature from that found in the crystalline metallic systems [17–19]. For specific dielectrics and alloys, a glassy state as a spin glass analog is driven by frustration and competing interaction, now called polar (dipolar and quadrupolar) and strain glasses [19,22–25].

* Corresponding author. Tel.: +82 2 3290 3098.
E-mail address: rscel@korea.ac.kr (C.E. Lee).

http://dx.doi.org/10.1016/j.ssc.2016.04.016
0038-1098/

The proton glass, classified as a subclass of dipole glass, is attained in the mixed crystals of $Rb_{1-x}(NH_4)_xH_2PO_4$ and $Rb_{1-x}(NH_4)_xH_2AsO_4$ due to the competing interaction between the ferroelectric ordering of RbH_2PO_4 (RbH_2AsO_4) and the antiferroelectric ordering of $NH_4H_2PO_4$ ($NH_4H_2AsO_4$) [19,23,24,26–28]. The disappearance of long-range order and the existence of short-range order within clusters are evidences of frozen-in state of protons. This proton glass transition shows frequency dispersion in its temperature-dependent dielectric constant and follow Vogel–Fulcher law. In this paper, we propose an alternative finite block pseudo-spin phenomenology of proton glass.

2. The finite block pseudo-spin theory

The nucleus of hydrogen(H)-bond nomenclature is the distinction between donor and acceptor. In any D−H···:A bond, D−H is the H-bond donor (and also a Brønsted acid, a Lewis acid, and an electron acceptor) and :A the H-bond acceptor (and also a Brønsted base, a Lewis base, and an electron donor) [29]. Hydrogen bonding occurs between a proton-donor group D−H and a proton-acceptor group A, where D is an electronegative atom, O, N, S, X (F, Cl, Br, I) or C, and the acceptor group is a lone pair of an electronegative atom or a π bond of a multiple bond (unsaturated) system. Generally, a H-bond can be characterized as a proton shared by two lone electron pairs. Therefore, we suppose that the subsystem of protons in H-bonded solids is composed of electron clusters, which may be regarded as finite block pseudo-spins [17–21].

For a proton glass comprised of random block pseudo-spins in the presence of an external electric field applied in the direction of the z-axis, the Hamiltonian $\mathscr{H}$ is given as [30]

$$\mathscr{H} = \sum_{i=1} \boxed{g}\mu_B \vec{H}\cdot\boxed{\vec{S}_i} = \boxed{g}\mu_B H \sum_{i=1} \boxed{S_{iz}} \tag{1}$$

where $\boxed{g}$ is the Lande's factor for a block pseudo-spin, μ_B is the Bohr magneton, and $\boxed{\vec{S}_i}$ is the spin operator for the i-th block pseudo-spin (describing the proton configurations in double potential wells) and the magnetic field H is substituted for the electric field

$$H \Rightarrow \frac{\beta_E}{\beta_H}\frac{eEL}{\mu_B} \tag{2}$$

and E is the electric field and L is the size of the sample. In Eq. (2), the phenomenological parameter eL corresponding to μ_B in magnetism has the dimension of the electric dipole moment.

The average number density of an electron in the absence of H is given by

$$\int_0^\infty f(\varepsilon)d\varepsilon = \int_0^\infty \frac{d\varepsilon}{1+\exp\frac{\varepsilon-\varepsilon_F}{k_BT}} = \int_0^\infty \frac{d\varepsilon}{1+\exp\frac{\varepsilon \pm \mu_B H \pm eEL \pm \hbar\omega - \varepsilon_F}{k_BT_{eff}}} \equiv k_BT\ln\left[1+\exp\frac{\varepsilon_F}{k_BT}\right] = k_BT_{eff}\ln\left[1+\exp\frac{-(\pm\mu_B H \pm eEL \pm \hbar\omega - \varepsilon_F)}{k_BT_{eff}}\right] \tag{3}$$

where $f(\varepsilon)$ is the Fermi–Dirac distribution, $N(\varepsilon)$ the density of states, andβ_i is a positive constant parameters as a substitution coefficient, and ε_F is the Fermi energy. Here considering that various energies can be converted to thermal temperature, the effective thermal temperature is given by

$$k_BT_{eff} \equiv k_BT \pm \beta_H\mu_B H \pm \beta_E eEL \pm \beta_\omega\hbar\omega. \tag{4}$$

The thermal expectation value of pseudo-magnetization (polarization in real dielectrics) is then given by

$$\begin{aligned} <M_z^E> &= -\boxed{g}eL\sum_i <\boxed{S_{iz}}> \\ &= -N_B\boxed{g}eL<\boxed{S_z}> \end{aligned} \tag{5}$$

where we assumed that $<\boxed{S_{iz}}>$ is independent of the block site i, and set it equal to $<\boxed{S_z}>$. Using Eq. (2), the thermal expectation value of the pseudo-magnetization is calculated as

$$\begin{aligned} <M_z^E> &= -N_B\boxed{g}eL\{\sum_{\boxed{S_z}=-S}^{S}\boxed{S_z}\exp[-\boxed{g}\frac{\beta_E}{\beta_H}eEL\boxed{S_z}/(k_BT)]\}/Z \\ Z &= \sum_{\boxed{S_z}=-S}^{S}\exp[-\boxed{g}\frac{\beta_E}{\beta_H}eEL\boxed{S_z}/(k_BT)] \\ S &= \delta(\frac{1}{2})N \end{aligned} \tag{6}$$

where N_B is the number of block pseudo-spins, N is the number of random spins in a block spin, and $\delta \approx 0$ represents an infinitesimal value.

The resulting thermal expectation value of the pseudo-magnetization and freezing temperature T_f (glass transition temperature T_g) are related by