Spin-Lattice Relaxation and Spatially Non-Uniforrn Fast Ionic Motion

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Dispersive motional relaxation of 19F nuclei in the superionic conductor beta-PbFz, Iightly doped with monovalent $I<+$ ions, i studied by nuclear magnetic resonance (NMR). A microscopic model of the spatially non-uniform motion of **'9** nnclei in this slightly disordered system, correctly predicts a wide range of observations which resemble glassy behavior. The model predicts tlie stretchecl exponential decay of the magnettzation in the rotating frame, the value of tlie exponent and its change when the doping level is varied, the scaling of the decays with temperature and rotating fielcl for a given doping level and the observed departures from simple relaxation theory.

Relaxation in disorderecl systems has attracted considerable interest in recent years mainly as a consequence of some universal features that appear to be associated with the phenomenon. Such is tlie case, for example, with tlie stretched exponential time dependence of the relaxation of form $\exp(-(t/\theta)^{\beta})$ with $0 \le \beta \le 1$, first introduced by Kohlrausch[1,2] to describe mechanical creep in glassy fibers, which has been found to be at least as ubiquitous and probably even more so than purely exponential relaxation[3]. Another characteristic feature of glassy systems is a non-Arrhenius behavior whereby correlation times are increasing more rapidly at low temperatures. The stretched exponential behavior could of course be explained in a simplistic way by assuming that in a disordered system there exists a probability distribution of relaxation times. If tlie overall time dependence of the process consists of additive contributions, one could obtain any desired time dependence by integrating over an heuristic probability

distribution. It has been pointed[4] that such an approach explains neither the universality of Kohlrausch's law nor its microscopic origin, therefore emphasizing the need of a more general approach. More recently[5,6] systematic clepartures from Kohlrauscli's law were observed in the higher frequency regime of the dielectric relaxation of various glassy systems. Even then, a universal scaling function was still found to correctly describe the relaxation for a wide range of frequency and temperature witli stretched exponential behavior still prevailing in the low frequency regime.

Although a variety of quite general concepts which may underlay the universality of dispersive relation in disordered and glassy systems have been proposed[4,7], few detailed microscopic models applicable to specific examples have been put forward. It has been proposed[6] that a convenient starting point for a microscopic theory may be found in the relaxation of systems clisplaying a simpler type of disorder than the one found

in structural glasses. Thus, orientationally disordered glasses for example, which have been shown to also exhibit universal features[6], may be more amenable to theoretical inodeling.

The superionic conductor $PbF_2^{[8,9]}$, doped with small amounts of KF may constitute another example of a system of this type. In this paper we present 60 MHz ^{19}F rotating frame nuclear spin-lattice relaxation (RFNSLR) measurements in the beta phase of PbF_2 doped with small amounts of KF. The data include temperature and rotating field dependences in crystals with two different concentrations of K^+. The fluorite beta phase of PbF_2 displays high anionic mobility reaching values typical of molten electrolytes at temperatures in the vicinity of 700 K. Moreover sufficient mobility to cause motional narrowing of the NMR line can be frozen in in PbF_2, even at temperatures as low as 200K, by the addition of small amounts of monovalent $(K^+, Na^+)^{[10]}$ or trivalent ions[11] such as Eu^{3+}.
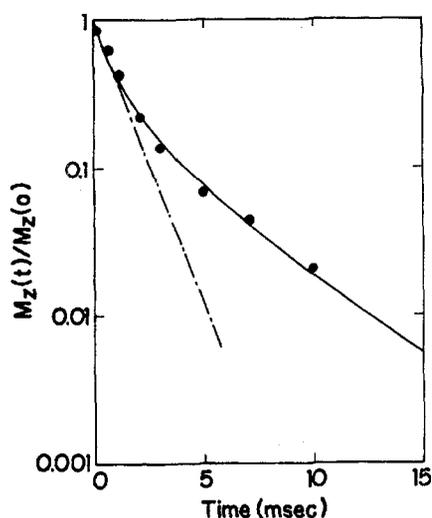
Figure 1. Decay of the rotating frame magnetization in beta-PbF_2 : K^+ (sample A) for $B_1 = 6.8$ gauss and $T = 198K$. The solid line was calculated from Eq.6 at $T = 197K$ with the two adjustable parameters used in all calculations: the fluoride vacancy prefactor $\tau_{v\infty} = 8.5 \times 10^{-14}$ sec and its activation energy $E, = 0.185$ ev/ion. The slope of the dashed line gives T_i,.
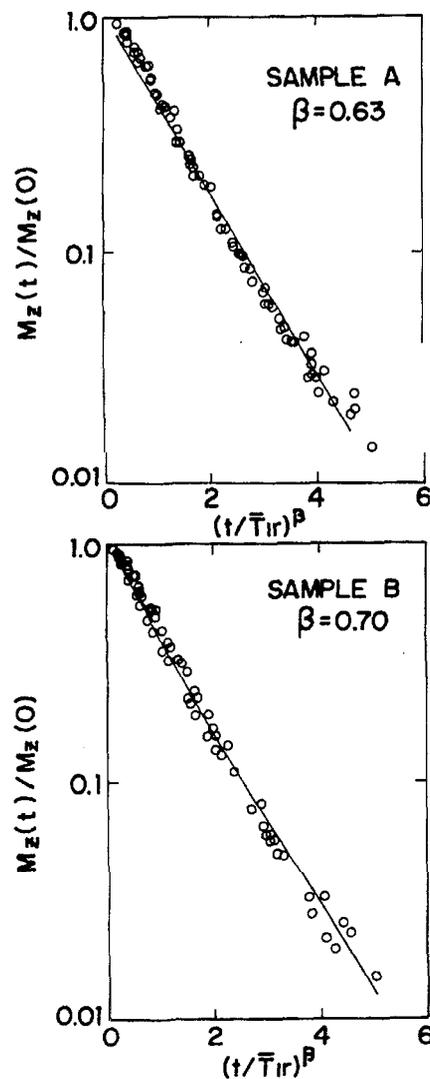
Figure 2. Scaling plots of the decays of the magnetization in the rotating frame for four values of B_1 and various temperatures in the range $178K < T < 253K$. The solid lines are theoretical fits from Eq.6. Fig.2a (top): scaling plot for sample A (0.054 mol % KF) as a function of reduced time $(t/\bar{T}_{1r})^\beta$ with $\beta = 0.63$. Fig.2b (bottom): scaling plot for sample B (0.0088 mol % KF) as a function of reduced time $(t/\bar{T}_{1r})^\beta$ with $\beta = 0.70$.

RFNSLR in pure PbF_2, at temperatures in the motionally narrowed line regime $(300K < T < 520K)$, appears to be well described, within the framework of the Bloembergen-Purcell-Pound (BPP) theory[9,12], by a single fluorine jump rate. In contrast, for $PbF_2 : K^+$ in a lower temperature range $(160K < T < 400K)$ but still corresponding to an equivalent motional regime, this description is no longer possible and a dispersive relaxation with a distribution of jump rates appears to prevail. Fig.1 shows a typical non exponential decay of the ^{19}F magnetization in the rotating frame for a radio-frquency field of amplitude $B_1 = 6.8$ gauss at T

$= 198K$ in a sainple containing 0.054 mol % KF (sample A). Tlie external magnetic field $\vec{B}_0$ was along [100]. Even though a rotating frame spin-lattice relaxation time cannot be defined in the usual way from data.such as those of Fig.1, it is still useful to introduce a characteristic time $\bar{T}_{1r}$, obtained froin tlie slope of tlie initial clecay shown by tlie dashed line of Fig.1. This permits a more concise description of tlie temperature and rotating field dependences of tlie relaxation rates also providing a scaling parameter to display the universality of tlie clecays.

Fig.2a shows tlie scaling of the decays for various teinperatures and rotating field amplitudes in sainple A wlien plotted as a.function of reduced time $(t/\bar{T}_{1r})^{0.63}$. Fig.2b shows decays for sample B (containing 0.0088 mol % of KF) exhibiting similar scaliiig when plotted as a function of $(t/\bar{T}_{1r})^{0.70}$. In Fig.3, tlie temperature dependence of $\bar{T}_{1r}$ for sample A is shown n.t two different values of B_1, whereas Fig.4 shows temperature dependence of T_{1r} in sainple A and sample B at a single value of B_1.
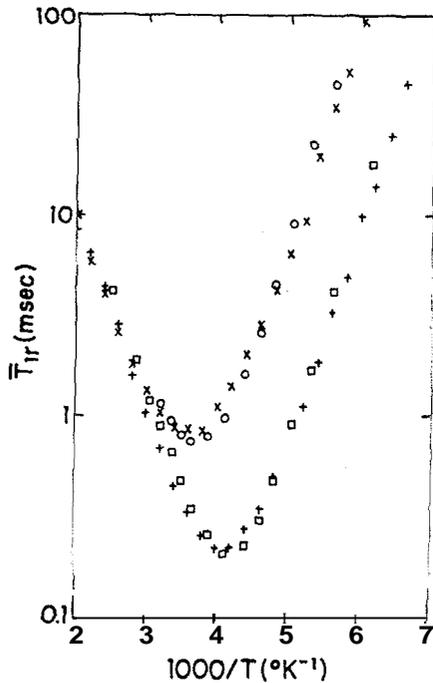
Figure 3. Experimental ($\square$) and tlieoretical (+) values of $\bar{T}_{1r}$ as a function of iiiverse temperature iii Sample A for $B_1 = 6.8$ gauss. Theoretical values were obtained from tlie decays of Eq.6 by the samc procedure outlined for tlie **experimental** data and shown by tlie dashed line of Fig.1. Experimental ($\bigcirc$) and tlieoretical ($\times$) values of $\bar{T}_{1r}$ are also shown for $B_1 = 25.0$ gauss. The slopes of tlie high temperature asymptotes are 0.18 ev/ion whereas the low temperature slopes are 0.24 ev/ion.

The experimental data of Fig.3 resemble the the-

oretical predictions of tlie BPP tlieory witli a single jump rate. Bowever, tlie asymptotes on hoth sides of tlie minima have cliffereiit slopes (0.18 ev/ion and 0.24 ev/ion). This could be interpreted as an apparent non-Arrhenius behavior witli tlie relaxation rate decreasing faster at low teinperatures. Furthermore, the rotating fielcl dependence ineasured at four different values of B_1 (6.8 G, 13.0 G, 18.9 G and 25.0 G), on tlie low temperature side of the ininima, yields $\bar{T}_{1r} \propto B_1^{1\ 78}$ instead of a quadratic dependence.
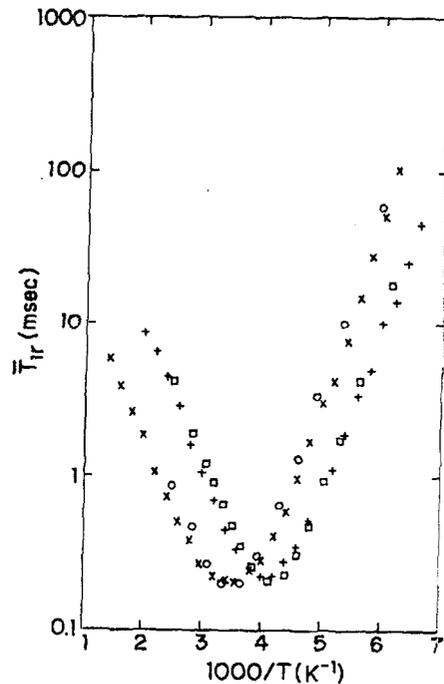
Figure 4. Experimental ($\square$) and tlieoretical (+) values of $\bar{T}_{1r}$ as a function of iiiverse temperatiire for $B_1 = 6.8$ gauss in Sample A. Theoretical values were obtained from Eq.6 by the same procedure used in Fig.3. Experimental ($\bigcirc$) and tlieoretical ($\times$) values of $\bar{T}_{1r}$ are also sliown for Sample B.

NMR probes tlie relaxation of ^{19}F magnetic moments caused by mobile defects, which in the present case, are fluoride vacancies created by doping with monovalent alkaline ions which substitute[13] for divalent Pb^{2+}. For this type of disorder, tlie probability distribution of ^{19}F residence times τ_F can be modeled. Consider a single K^+ ion substituting for Pb^{2+} at tlie center of a sphere of radius R containing inany fluorine nuclei and let r be tlie radial distance from tlie K^+ ion to a charge-compensating fluoride vacancy (F_ν). Neglecting thermally induced defects in the temperature range of tlie experiment, the motion of fluorine nuclei

can be assumed to be controlled by the spatially non-uniform probability distribution of fluoricle F_ν vacaiicies. At low temperatiires, and because of tlie Coulombhic attractioii binding $K^+ : F_\nu$ pairs, fluoride vacancies can be found witli significant probability only for small values of r and fluorine motion only talíes place in tlie vicinity of the doping ions. As the teinperature increases and tlie $K^+ : F_\nu$ pairs clissociate, a larger fraction of fluorines become mobile.

Denoting by $P(r,T)4\pi r^2 dr$ tlie probability of finding a fluoride vacancy witliin a spherical shell of radius' between r and $r + dr$ and by $n_F 4\pi r^2 dr$ tlie number of fluorine nuclei within tlie same volume, tlie jump rate $1/\tau_F$ of a fluoriiie can be related to tlie jump rate $1/\tau_\nu$ of tlie vacancy by:

$$1/\tau_F = (P(r,T)/n_F)(1/\tau_\nu) , \qquad (1)$$

wliere $n_F = 3.778 \times 10^{22} \text{cm}^{-3}$ is tlie number of fluorines per unit voluine. Furthermore, tlie fluoricle vacancy motion within the sphere or radius R is assumed to be characterized by a single resiclence tiine witli an *Arrhenius* dependence oii temperature as $\text{r}, = \text{r}_{\infty} \exp(E_\nu/kT)$.

For the proposecl model of bound $K^+ : F_\nu$ pairs, tlie probability density $P(r,\text{t})$ can be writteii as:

$$P(r,T) = e^{-\Phi/kT} / \int_\Omega e^{-\Phi/kT} d\Omega \qquad (2)$$

where $\Phi(r,T)$ is tlie potential eiiergy of a fluoride vacancy at a distance r from a K^+ dopant and tlie integral extends over the volume Ω_a of a spliere of influence suirounding a siiigle K^+ ion.

The Coulomb attractioii between tlie effective positive charge of a fluoride vacancy and tlie effective negative cliarge of a monovalent dopant ioii is shielded by tlie ionic atmosphere. For the relatively low concentration of mobile defects in our samples, the net effect can be described by a simple Debye-Hückel[14,10] potential:

$$\Phi(r,T) = -[e^{\lambda b}/(1+\lambda b)](q^2/\epsilon r)e^{-\lambda r} , \qquad (3)$$

wliere $\lambda = (6q^2/\epsilon k T R^3)^{1/2}$, q is tlie electronic cliarge, $\epsilon \cong 30$ is tlie large static dielectric constant of this superionic conductor, R denotes the radius of a sphere containing a, single dopant ioii and b is the distance of closest approach between tlie fluoride vacancy and tlie K^+ ion. For tlie fluorite structure of beta-PbF_2, $b = 2.58$Å. We further assume tliat eacli ^{19}F is relaxed clirectly by tlie fluctuating dipolar fields of neighboriiig mobile nuclei and tliat spin diffusion between more distant nuclei within a sphere of iiifluence is slow compared witli direct RFNSLR rates. For a ^{19}F spin at a distance r from tlie center of a sphere of influence, tlie rotating frame relaxation rate $1/T_{1r}$ predicted by the BPP tlieory is tlien giveii by[9]:

$$1/T_{1r} = W\tau_F(\text{r},T)/[1 + 4\omega_1^2\tau_F^2(r,T)] , \qquad (4)$$

wliere $\omega_1 = \gamma_F B_1$ ($\gamma_F = 2.5166 \times 10^4$ gauss/sec) and $W = 0.44 \times 10^{10}\text{sec}^{-2}$ is approximately equal to tlie rigid lattice contribution to tlie seconcl moment.

The time evolution of tlie magnetization parallel to $\vec{B}_1$ (along z), can be obtained from Eq. 4 by adding the coiitributions from all nuclei within tlie sphere of radius R containing a single dopant ion. Bowever, giveii the disorder introcluced by the random nature of tlie dopiiig process, tlie radius R must be regarded as a random variable with a probability density $Q(R)$ to be determined. Since tlie substitution of sites by a given average concentration of dopants can be expected to follow a binomial distribution, tlie probability that a sphere of radius R contains a single dopant ion can be calculated. Moreover if tlie spliere of radius R contains many Pb^{2+} sites witli very small K^+ occupation probability, as in tlie present case, tlie binomial distribution becomes, to a very good approximation, a Poisson distribution. The probability tliat a.sphere containing a single K^+ ioii has a.radius between R and R $+ dR$, is then given by:

$$Q(R)dR = 4\pi R^2 n_d e^{-n_d(4/3)\pi R^3} dR / \left(\int_b^\infty 4\pi \rho^2 n_d e^{-n_d(4/3)\pi \rho^3} d\rho \right) \qquad (5)$$

The final time evolutioii of the overall rotating frame magnetization $M_z(t)$,averaged over the Poisson distribution $Q(R)$, can be obtained from Eqs.1-5:

$$M_z(t)/M_z(0) = \int_b^\infty Q(R) \left\{ [(3/4\pi)(R^3 - b^3)^{-1}] \int_b^R e^{-t/T_{1r}} 4\pi r^2 dr \right\} dR . \tag{6}$$

Various comparisons between the predictions of Eq.6 and the experimental data are shown in Figs.1-4 where the only two adjustable parameters were $\tau_{\nu\infty} = 8.5 \times 10^{-14}$sec and $E = 0.185$ ev/ion. The average number of dopants per unit volume n_d was obtained from the known concentrations of Samples A and B and is better represented by an average radius $R = [3/(4\pi n_d)]^{1/3}$. For sample A, $\bar{R}_A = 30.4$Å while for sample B, $\bar{R}_B = 55.3$Å, whereas the shielding length of Eq. 3 is $(\bar{\lambda}_A)^{-1} \approx \bar{R}_A/2$ for sample A at $T = 273K$.

Fig. 1 shows a typical theoretical decay obtained by a numerical integration of Eq.6 for $T = 197K$ and $B_1 = 6.8$ gauss in sample A. Figs. 2a and 2b show theoretical decays with $\beta = 0.63$ (sample A) and $\beta = 0.70$ (sample B) which also exhibit the scaling behavior with respect to temperature and rotating field amplitude found experimentally. Fig. 2b shows that β actually becomes closer to one as the degree of disorder is reduced.

Figs.3-4 show calculated values of $\bar{T}_{1r}$ where each point is obtained by first computing the decay from Eq.6 and subsequently determining the time constant $\bar{T}_{1r}$ by the procedure outlined in Fig.1.

The model yields the correct values of the exponent β for two different values of the concentration of dopants and accounts for the observed scaling with temperature and B_1 (Fig.2). It also quantitatively explains the shift in the temperature dependence of T_{1r} with concentration (Fig.4) as well as the observed departures from simple relaxation theory (Fig.3). Given the agreement between this wide range of data and the predictions of Eq.6 we conclude that a fairly complete microscopic description of dispersive motional relaxation caused by this type of mild disorder is possiblt:. This may provide some clues for understanding the dynamics of glassy systems. The Poisson distribution, applicable to the dilute disorder prevailing here, leads naturally to Kohlraush relaxation of universal type under quite general conditions. This can also be verified analytically using the method of steepest descent to calculate, for simpler cases, the asymptotic behavior of integral such as that of Eq.6. The values of the exponents are determined not only by the degree of disorder but also by the spatial variation of the potential (Debye-Hckel) which for low temperatures, confines the motion of the magnetic dipole moments to localized regions around the randomly distributed centers.

Acknowledgments

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