

Detection by double-modulation ESR spectroscopy of millisecond-range polarization fluctuations and Vogel-Fulcher behavior in partially deuterated potassium dihydrogen phosphate

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Measurements of polarization fluctuations at time scales longer than 10^{-6} s have not been feasible via electron spin resonance techniques. Using partially deuterated KH_2PO_4 (KDP) as an example, this study shows that the double-modulation electron spin resonance technique enables the detection of polarization fluctuations on the millisecond time scale. The measured correlation times for 73% deuterated KDP exhibit Vogel-Fulcher behavior, indicating that this lattice may exhibit *structural glass* behavior, with a glass formation temperature of 138 ± 10 K.

This work reports on a new application of double-modulation electron spin resonance (DMESR):¹⁻⁸ measurement of millisecond-range local polarization fluctuations in ferroelectric materials. The procedure is illustrated via measurements of such fluctuations in the ferroelectric phase of $\sim 73\%$ deuterated KH_2PO_4 (KDP), utilizing the SeO_4^{3-} center⁹⁻¹⁵ as a spin probe. Partially deuterated KDP was selected for this study because this lattice affords sharper ESR signals than normal KDP, owing to the absence of proton superhyperfine splittings in the former. The SeO_4^{3-} center was utilized as a probe because numerous earlier ESR and electron nuclear double-resonance (ENDOR) studies⁹⁻¹⁵ have established that, compared to other probes used in such studies (e.g., AsO_4^{4-} , CrO_4^{3-} , or MoO_4^{3-} radicals, Ti^{2+} center), the SeO_4^{3-} radical best approximates the overall electric charge and local symmetry of the PO_4^{3-} unit. The SeO_4^{3-} is also preferred because the most abundant isotopes of Se (^{76,78,80,82}Se, 92% abundance) have nuclear spin $I=0$, hence the SeO_4^{3-} center can be analyzed via an effective electronic spin- $\frac{1}{2}$ system, unlike the case with the other probes (e.g., AsO_4^{4-} , Ti^{2+} , Hg^+) for which hyperfine effects dominate the ESR spectra. However, in spite of these numerous earlier ESR and ENDOR studies⁹⁻¹⁵ it has thus far not been feasible to measure (in KDP) polarization fluctuations at rates longer than the microsecond range. The existence of such "slow" fluctuations has been indicated by earlier dielectric measurements of KDP, deuterated KDP,¹⁶⁻¹⁸ and the RbH_2PO_4 - $\text{NH}_4\text{H}_2\text{PO}_4$ proton glasses.¹⁹⁻²¹ The primary goal of this undertaking was to examine the feasibility of detecting such slow local fluctuations via the DMESR technique which is a simple variant of conventional ESR, but exhibits sensitivity to slower molecular motion.¹⁻⁸ If successful, the DMESR technique has several advantages over dielectric relaxation, in particular, for powdered samples, and for directly identifying the ionic units involved in the fluctuations. Our secondary goal was to investigate the local dynamics of H (D) in the ferroelectric phase at $T \ll T_c$, where experimental data are scarce.

In the DMESR technique¹⁻⁸ one observes a change in the intensity of the standard, first-derivative, ESR signal (detected with 100-kHz Zeeman field modulation) caused by the application of an additional (variable frequency) Zeeman field modulation. The Zeeman field itself is kept fixed at the position of the peak of any (generally the strongest) component of an ESR multiplet. The height of the monitored peak exhibits a sharp change whenever the frequency of the second modulation, labeled as ν_2 (c.f. Fig. 1), becomes an exact multiple of the frequency of the first modulation (100 kHz). The DMESR signal is thus a plot of the change in the ESR signal versus ν_2 . The observed width of a typical DMESR peak is only a few tens of kHz, which is some 3 orders of magnitude narrower than the width of the corresponding ESR peak (~ 5 – 10 G or 15–30 MHz). While the mechanism of this line narrowing process is not yet fully understood, recent theoret-

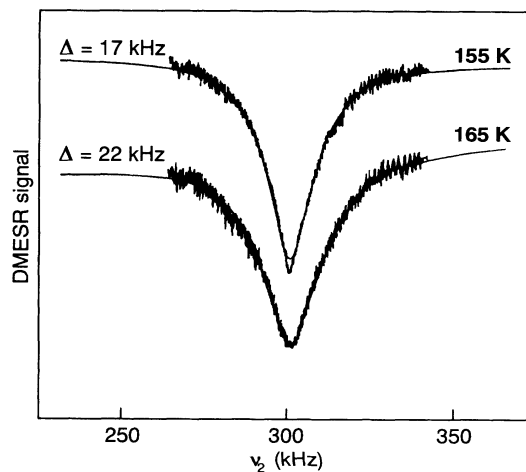


FIG. 1. Typical DMESR signals from 73% deuterated $\text{KD}_2\text{PO}_4:\text{SeO}_4^{3-}$ at the indicated temperatures of 155 and 165 K. The solid line represents the best fit to a Lorentzian line shape function with the width at half intensity (Δ) as indicated.

ical⁵ as well as experimental studies^{4,6-8} indicate that the DMESR enhancement is related to the spin-lattice relaxation (T_1) process of the individual spin packets comprising an inhomogeneously broadened ESR signal. These studies show⁵ that the DMESR linewidth, $(\Delta)_{DM}$, is given by

$$(\Delta)_{DM} = \frac{1}{\pi T_1} \quad \text{for } T_1 \gg T_2, \quad (1)$$

where T_1 and T_2 correspond, respectively, to the spin-lattice and spin-spin relaxation times of typical spin packets comprising the corresponding inhomogeneously broadened ESR signal. The sensitivity of this method was recently demonstrated⁸ by T_1 measurement for $\text{KH}_2\text{AsO}_4:\text{AsO}_4^{4-}$. The data show good agreement with T_1 data as deduced by employing the electron spin-echo method. For dilute paramagnets, such as our sample of partially deuterated KDP doped with SeO_4^{3-} , T_1 is generally much longer than T_2 , hence Eq. (1) is quite valid. This fact also implies that $(\Delta)_{DM} \ll (\Delta)_{ENDOR}$ because ENDOR linewidths correspond approximately to the T_2^{-1} value of a spin packet. The T_1 values calculated from the DMESR linewidths make it possible to estimate the correlation time τ for the molecular reorientations involved in the T_1 phenomenon. This is accomplished by assuming that the rate of fluctuations causing the relaxation is in the "slow" motion regime of the modified Bloch equation.²² This approximation is well justified because in the temperature region where DMESR peaks broaden significantly, ESR-ENDOR signals exhibit no change. By analogy to standard ESR, and using the modified Bloch equation in the slow motion limit,²² one can phenomenologically relate the broadening of the DMESR peaks to the correlation time τ via the relation

$$\Delta_{DM}(T) = \Delta_{DM}(0) + \frac{1}{\pi\tau}, \quad (2)$$

where $\Delta_{DM}(0)$ corresponds to the value of Δ_{DM} in the frozen motion limit. Equation (2) expresses essentially the spin "lifetime broadening" concept,²² and was here utilized for measuring the τ values.

The single crystals investigated here were grown from saturated solutions of KH_2PO_4 in D_2O containing about 1% K_2SeO_4 . The crystals grew as rectangular plates, with their c axis elongated, and were γ irradiated to a dose of a few MRad (not critical) to generate the SeO_4^{3-} ions. The T_c of these samples was measured as 201 K via ESR signal splitting,¹⁴ as well as microwave loss data.²³ This T_c corresponds to a deuteration level of $73 \pm 5\%$ as deduced from the formula T_c (K) = $123 + 101x$, where x is the fraction of deuterons.²⁴

All ESR and ENDOR measurements were made utilizing a high rf power ENDOR spectrometer described recently.^{25,26} DMESR signals were measured using a Varian E-109 X-band ESR spectrometer utilizing 100 kHz as the basic Zeeman field modulation, with provision for an additional, variable frequency Zeeman modulation.^{1,3,6-8} The source of the second modulation frequency, ν_2 , was a Wavetek frequency synthesizer. The DMESR signals were recorded using a signal averager whose time base

was triggered by the Wavetek generator, while its input was derived from the output of the ESR spectrometer.

The ESR spectra of the SeO_4^{3-} center in KD_2PO_4 , DKDP, have been well documented.⁹⁻¹⁵ Briefly, the dominant features arise from the $^{76,78,80}\text{Se}$ ($I=0$) isotopes, i.e., a multiplet at approximately the free-electron g value of 2.00. In the paraelectric phase, the ESR spectrum consists of a single peak whose width is determined by the rate of polarization fluctuations, $\approx 10^8$ Hz at a few degrees above T_c .^{9-15,27-30} Below T_c , however, the fluctuations become too slow to be measured by ESR or ENDOR, and each signal splits into a doublet due to the lowering of symmetry and formation of local ferroelectric domains.¹⁴ Utilization of externally applied electric fields^{27,28} enabled us to assign components belonging a given domain (+ or -). This is the temperature regime where the DMESR methodology was found to be effective for measuring the τ whereas ESR as well as ENDOR were not.

Figure 1 shows typical DMESR peaks from DKDP: SeO_4^{3-} in the ferroelectric phase, at temperatures of 155 K (top) and 165 K (bottom). Both peaks showed satisfactory fit to a Lorentzian line shape, as expected from theoretical models.⁵ The solid curves in Fig. 1 are the fitted Lorentzian functions, with the width Δ_{DM} as marked. It can be noted that Δ_{DM} for 165 K (22 kHz) is larger than that for 155 K (17 kHz). This was also found to be the case at other temperatures, as shown in Fig. 2 where we have plotted $\pi\Delta_{DM} (\approx T_1^{-1})$ versus temperature T on log-log scale. In addition, the two dotted lines are shown that represent linear and quadratic temperature dependence as marked. The plot exhibits two regions of temperature dependence: a monotonic increase with increasing temperature up to about 160 K, but deviation from this behavior at higher temperatures. Earlier measurements^{31,32} of relaxation rates in similar ferroelectric systems such as KDP using SeO_4^{3-} and AsO_4^{4-} probes as

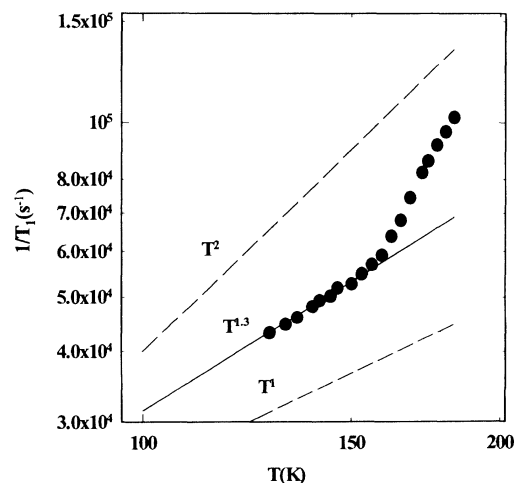


FIG. 2. Temperature dependence of the DMESR linewidth, $\pi\Delta_{DM} (\approx T_1^{-1})$ from 73% deuterated $\text{KD}_2\text{PO}_4:\text{SeO}_4^{3-}$. The solid line represents the best fit to the temperature dependence for data in the low-temperature region.

well as KDA with AsO_4^{4-} as a probe, show similar monotonic increasing behavior at temperatures below T_c . According to these studies^{31,32} the dominant contribution to relaxation rates at high temperature (≈ 130 K) can be described only by a two-phonon Raman process³² or by Raman processes with acoustic and optic phonons as follows:³¹

$$\frac{1}{T_1} = AT + C_n T^{n+1} I_n(\theta/T) / I_n(\infty) + B \operatorname{csch}^2(E_0/2T), \quad (3)$$

where $I_n(\theta/T)$ is the transport integral

$$I_n = \left(\frac{1}{4}\right) \int_0^{k\theta/h} \nu^n \operatorname{csch}^2(h\nu/2kT) d\nu, \quad (4)$$

and A , C_n , and B are parameters. The first two terms describe contributions of the acoustic phonons in direct process and Raman process with Debye temperature θ , while the third term describes contribution of the optical phonon branch with energy E_0 . As is well known, at temperature well below θ two-phonon Raman processes usually dominate the relaxation of spins in crystalline lattices and lead to $T_1^{-1} \propto T^m$, where $m=7$ or 9 depending on the details of the spin system and the relaxation process. However, for $T/\theta > 0.5$, at higher temperatures T_1^{-1} increases as T^2 . θ was found to be 90 K for KDA (Ref. 31) and 119 K for KDP (Ref. 32) from T_1 data employing relation (3). Thus, for DKDP one would expect a T^2 temperature dependence in the investigated temperature regime ($T > \theta$). This is also the case for the optical phonon model where one expects in the high-temperature limit either an exponential or (for, $E_0 \ll kT$) T^2 temperature dependence. For the T_1 values measured here for DKDP the low-temperature data exhibited as $T^{-1} \propto T^{1.3}$ (as shown in Fig. 2), indicating that the contribution of only a simple two-phonon process (3) is insufficient here. There are several types of relaxation processes which can dominate at high temperature and which can lead to $T^{-1} \propto T$. These relaxation processes usually have origin in low-lying vibrational states and are often associated with excitation of two-level systems, TLS.^{33,34} The TLS mechanism leads to transitions between levels by phonon-associated tunneling and to spin flips by modulating the spin-orbit or hyperfine interaction.^{33,34} While these questions are highly interesting, for the present study, we focused on a novel feature, a decrease in T_1 faster than given by the T^2 dependence starting at about 160 K. In order to isolate this additional contribution to T_1 , we subtracted the expected $T^{1.3}$ contribution of the low-temperature mechanism at higher temperatures (presented as the solid line in Fig. 2) from the experimental values for that temperature region. The obtained Δ_{DM} values were then converted to τ via Eq. (2), and these τ values are shown as the solid circles in Fig. 3. It will be noted that Fig. 3 is an Arrhenius plot, i.e., a plot of $\ln \tau$ versus $1/T$. It can be also seen from this figure that these data points do not fall on a straight line, hence the underlying motion cannot be defined by the Arrhenius equation $\tau = \tau_0 \exp(E/kT)$, with a temperature-independent activation energy E .

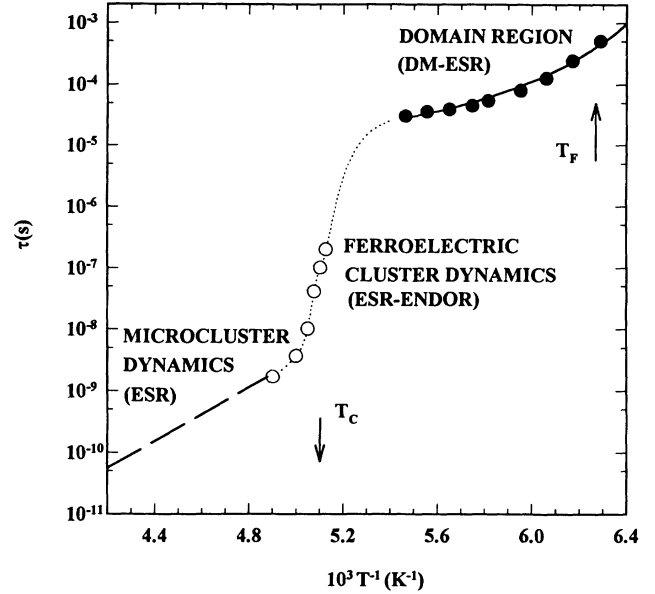


FIG. 3. An Arrhenius plot of the correlation time τ of polarization fluctuations in 73% deuterated KD_2PO_4 as measured by ESR and ENDOR (\circ) and DMESR (\bullet). The dotted line represents the data from earlier ESR measurements (Refs. 29 and 30). The solid curve through the solid circles (\bullet) is the best fit to the Vogel-Fulcher relationship. The dotted line through the open circles (\circ) is just a guide to the eye.

Our attempts to understand the origin of nonlinearity in the above discussed plot led us to try to fit these data points to the Vogel-Fulcher relation.^{19–21} Such a behavior had in fact been indicated by earlier dielectric relaxation studies^{17–18} in KDP as well as DKDP in their ferroelectric phase. We thus fitted these data to the Vogel-Fulcher equation of the form

$$\tau = \tau_0 \exp[\bar{E}/(T - T_0)]. \quad (5)$$

The Vogel-Fulcher equation implies that the sample exhibits some sort of “glass” formation, with T_0 as the glass freezing temperature at which $\tau \rightarrow \infty$. The activation energy \bar{E} is a Gaussian average of the activation energies corresponding to different “cluster” sizes in the glass. The solid curve in Fig. 3 corresponds to the best fit of the experimental data points to the Vogel-Fulcher relationship, with $\bar{E} = 109 \pm 10$ K, $T_0 \approx 138 \pm 10$ K, and $\tau_0 \approx 2 \times 10^{-6}$ s. These values should be compared to those obtained from dielectric measurements on a 69% deuterated KDP crystal.²⁴ $\bar{E} = 109$ K, $T_0 = 137$ K, and $\tau_0 \approx 10^{-9}$ s. The agreement between the DMESR and dielectric data is good for \bar{E} and T_0 . We note, however, that the τ values obtained from DMESR are much larger. We tentatively ascribe this difference to the fact that ESR and, hence, DMESR observations will be dominated by polarization fluctuations of the local domain environment around the probe, whereas dielectric loss data are thought to correspond to fluctuations of molecular dipoles at the domain walls,^{17,18} which might be expected to be faster than the dipoles in the bulk, but this conjecture is only tentative. Nevertheless, together with the

earlier reported τ values as measured via ESR and ENDOR,^{9-15,29,30} inclusion of the DMESR data has now made it possible to measure the correlation time for the polarization fluctuations in a KDP-type crystal in both paraelectric and ferroelectric phases, via ESR methodologies. Note that τ has been measured over a range of 5 orders of magnitude (Fig. 3). As reported earlier^{27,28} the correlation time τ follows an Arrhenius behavior in the paraelectric phase, as shown by the dotted line. As $T \rightarrow T_c$, however, τ increases rapidly as the size of the ferroelectric clusters increases. This time scale of 10^{-7} – 10^{-6} s was probed with ENDOR.^{25,26} Finally at about 60 K below T_c , τ increased rapidly to about

10^{-4} – 10^{-3} s and became too large to be measured even with DMESR. We tentatively ascribe this phenomenon to the rapid growth of local domains and some sort of structural glass formation as the proton-deuteron lattice stiffens. It may be recalled that our interpretation of τ as the polarization fluctuation time follows directly from the identification of domain splitting²⁷ of the ESR lines on which the DMESR measurements were made.

To summarize, this study demonstrates that the DMESR technique can be utilized to detect very slow (millisecond-range) polarization fluctuations in ferroelectrics, something that has not been possible via ESR and ENDOR measurements.^{13,14,25-30}

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