Evidence for Spin-Fracton Relaxation in the Polymer Resin P4VP Doped with Kramers Ions Co²⁺, Nd³⁺, and Yb³⁺

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An analysis of the temperature dependency of the relaxation rate (T_1^{-1}) in three poly-4-vinylpyridine (P4VP) resin samples, possessing fractal structure, doped with the Kramers ions Co²⁺, Yb³⁺, and Nd³⁺, indicated spin-fracton relaxation over the 4.2–20 K range consistent with the Raman process involving two-fracton inelastic scattering characterized by high localization.

Research on amorphous systems has intensified over the last two decades with the discovery of fractal character of these materials. The nature of thermal vibrations in these systems has not yet been fully understood. Original experimental studies on amorphous materials using Brillouin scattering and Raman spectroscopy [1], were later extended to study of coupling of spins with the vibrational modes of lattice: extended, or localized, phonons. A novel comprehensive theory of spin relaxation in the presence of fractons, or localized phonons, was developed by Alexander, Entin-Wohlman, and Orbach [2–5]. Although experimental confirmation of spin-fracton relaxation has been achieved, to some extent, by nuclear quadrupole resonance (NQR) [6], it has not so far been accomplished by EPR to our knowledge. The purpose of this Letter is to report such a verification, accomplished by analyzing the measured temperature dependency of the relaxation rate, T_1^{-1}, where T_1 is the spin-lattice relaxation time (SLRT), in three cross-linked resin polymer P4VP (poly-4-vinylpyridine) samples, possessing fractal character at low temperatures, doped by the Co²⁺, Nd³⁺, and Yb³⁺ Kramers rare-earth ions possessing strong spin-orbit couplings.

Earlier measurements on amorphous systems exhibited the dependencies $T_1^{-1} \propto T^2$ and T at low and intermediate temperatures, respectively [7,8], mainly explained by invoking TLS (two-level tunneling states) centers [9]. On the other hand, the observed $T^{6.6}$ dependency of T_1^{-1} in biomolecules by Stapleton *et al.* [10] indicated that mechanisms other than that due to TLS centers could be responsible for relaxation.

Several conditions must be fulfilled simultaneously to observe spin-fracton relaxation by EPR: (i) The sample must possess fractal structure [11]. (ii) It should be doped with paramagnetic ions possessing large spin-orbit coupling in order that the mechanisms of relaxation by modulation of ligand fields by fractons (or phonons) can be monitored sensitively [11]. (iii) One is able to measure very short relaxation times, typical of ions possessing large spin-orbit couplings.

In this study, three cross-linked resin polymer P4VP (poly-4-vinylpyridine) samples were chosen, possessing fractal structures [12]. They were doped by CoCl₂ (2 wt %), NdCl₃ (0.8 wt %), and YbCl₃ (0.5 wt %). The relaxation times were here measured by the "modulation" method [13,14], which utilizes an amplitude-modulated microwave field and a pickup coil coaxial with the external magnetic field, capable of measuring relaxation times in the range $10^{-10} < T_1 < 10^{-6}$ s. In the presence of either weak signal or wide EPR line, the range of measurement is restricted to about 10^{-6}–10^{-8} s. Measurement of such short relaxation times thus requires use of samples relatively highly doped by paramagnetic ions in order to obtain sufficiently strong signals.

I. Experimental results.—(a) Sample doped with CoCl₂: The observed temperature dependency of the relaxation rate is exhibited in Fig. 1. The investigated temperature range was restricted to 4.2–20 K, due to both weak signal and rapid relaxation (wider EPR line). The relaxation rate is well described by the relation $T_1^{-1} \propto T^n$. The best fit to the experimental curve [15] yielded $n = 3.85 \pm 0.35$ in the temperature interval 11–19 K. (b) Samples doped with NdCl₃ and YbCl₃: The observed dependencies $T_1^{-1}(T)$ are shown in Figs. 2 and 3, respectively. Because of the weak signals, measurements of SLRT with these relatively small concentrations of Yb³⁺ and Nd³⁺ ions were somewhat more difficult. They could be obtained only over the ranges 4.2–20 K and 11–18 K for the samples doped with Nd³⁺ and Yb³⁺ ions, respectively. The best fit to experimental data to $T_1^{-1} \propto T^n$ provided the following values [15]: $n = 3.25 \pm 0.55$ for the sample doped with NdCl₃ over the 13–20 K range, and $n = 5.35 \pm 0.55$ for the sample doped with YbCl₃ over the 13–18 K range. (c) Effect of magnetic interactions: Effect of exchange interactions among paramagnetic ions on spin-lattice relaxation, if dominant, would be to bring a temperature dependency of the relaxation rate as $T^n (n = 1 + \eta; \ 0 \leq \eta < 1)$ [16], which is clearly weaker than the ones actually observed here. Further, the role of exchange interaction in the samples studied here is to diminish the relaxation rate for greater concentration of ions, contrary to the fact that in the present case the value of n (= 3.25) for the less
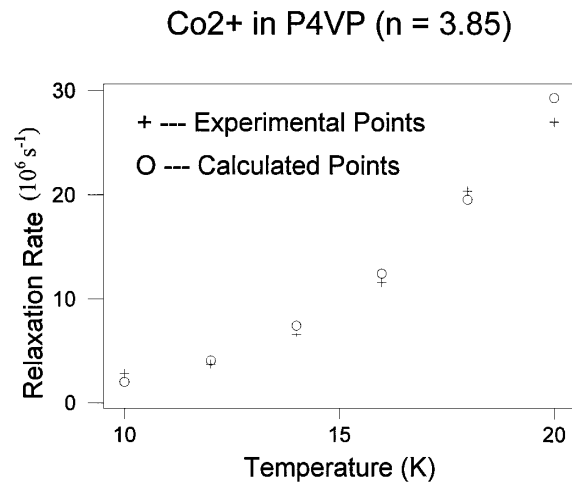
Co2+ in P4VP (n = 3.85)

FIG. 1. Dependency of the observed (+) relaxation rate (T_1^{-1}) upon temperature of a P4VP sample doped by 2% of CoCl$_2$. The experimental data are well described by the theoretical curve ($\circ$): $T_1^{-1} \propto T^n$, with $n = 3.85 \pm 0.35$ between 10 and 19 K. (The data indicate that the relaxation rate decreases very slowly below 10 K.) The value of the parameter R^2, defining statistically the goodness of fit, is $R^2 = 0.980$, where $R^2 \equiv \sum_i (Y_{exp}^i - Y_{ave})^2 / (Y_{calc}^i - Y_{ave})^2$, where Y stands for $\log(T_1^{-1})$, and the subscripts exp, calc, and ave represent the experimental, calculated, and average values, respectively, while the superscript i represents the ith data point. Thus, the fit is the best when $R^2 = 1$. The error in T_1 measurement is 6% and the precision in temperature measurement is ± 0.1 K. (The size of data points *do not* represent experimental errors.)

concentrated sample doped with Nd^{3+} (0.8%) is smaller than that ($n = 3.85$) in the more concentrated sample with Co^{2+} (2.0%). The relaxation rate of P4VP doped by 2.8% of CuCl$_2$ was reported to exhibit a relaxation rate of 4×10^6 s^{-1} at 20 K [11], which is 7.5 times smaller than 30×10^6 s^{-1} at 20 K, exhibited by the P4VP sample doped with the less concentrated (2.0 wt %) CoCl$_2$ reported here. It is then concluded that the exchange interaction has a negligible effect as compared with the other mechanism of relaxation prevalent in the samples studied here, specifically the two-phonon Raman spin-fracton relaxation process described below.

II. Interpretation of data.—Spin-fracton relaxation: The use of three complementary techniques (i) small-angle x-ray scattering, (ii) NMR with pulsed field gradients, and (iii) nuclear relaxation in the presence of paramagnetic ions confirmed that P4VP, indeed, possesses fractal structure [12]. For spin-fracton relaxation of Kramers ions, involving a Raman process with two-fracton inelastic scattering when there exists high localization [2,3,5], the relaxation rate can be expressed as [2,3]

$$T_1^{-1} \propto T^n, \qquad (1)$$

with

$$n = 2\bar{\bar{d}}(1 + 2d_\varphi/D) - 1, \qquad (2)$$
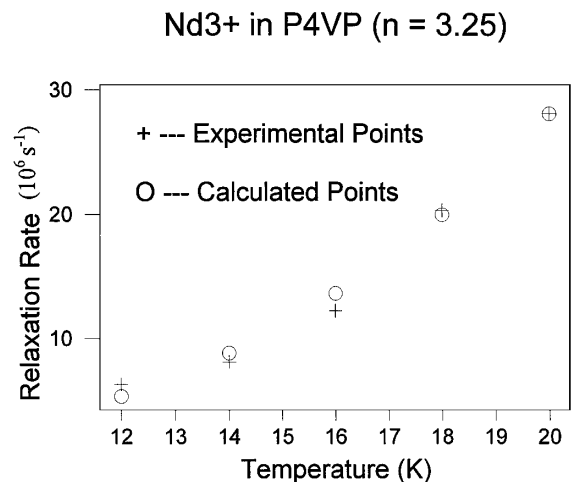
Nd3+ in P4VP (n = 3.25)

FIG. 2. Dependency of the observed (+) relaxation rate (T_1^{-1}) upon temperature of a P4VP sample doped by 0.8% of NdCl$_3$. The experimental data are well accounted for by the theoretical curve ($\circ$): $T_1^{-1} \propto T^n$, with $n = 3.25 \pm 0.55$ between 12 and 20 K: $R^2 = 0.982$. (The data indicate that the relaxation rate decreases very slowly below 12 K.) Other details and errors are the same as those indicated in the caption of Fig. 1.

where, $\bar{\bar{d}}$, d_φ, and D denote, respectively, fracton dimensionality, a parameter defined by the range dependency of the fracton wave function [2], and fractal dimensionality. Using the value $\bar{\bar{d}} = 1.33$ as calculated for a percolating network [2,3] and $D/d_\varphi = 1.8$ [2,3,12], one obtains $n = 4.63$. Conversely, the value of $\bar{\bar{d}}$ can be found from the measured value of n via the temperature dependency of the relaxation rate, provided that the value of D/d_φ is known. Using now the same value of $D/d_\varphi (= 1.8)$ for P4VP as that adopted by Chachaty *et al.* [12], and by Alexander *et al.* [2,3], in conjunction with the values of n
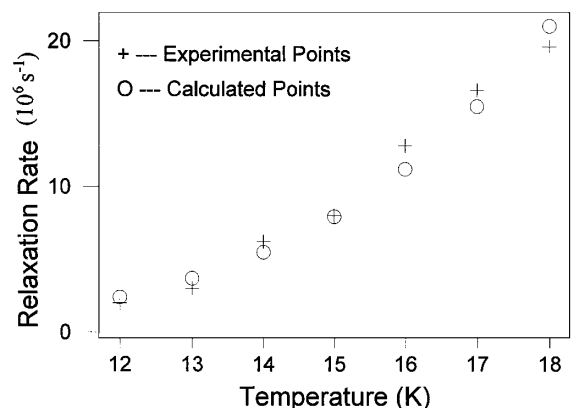
Yb3+ in P4VP (n=5.35)

FIG. 3. Dependency of the observed (+) relaxation rate (T_1^{-1}) upon temperature of a P4VP sample doped by 0.5% YbCl$_3$. The experimental data are well accounted for by the theoretical curve ($\circ$): $T_1^{-1} \propto T^n$, with $n = 5.35 \pm 0.55$ between 12 and 18 K: $R^2 = 0.978$. (There are no data available below 12 K.) Other details and errors are the same as those indicated in the caption of Fig. 1.

drawn from relaxation-time measurements on P4VP samples doped with Co^{2+}, Yb^{3+}, and Nd^{3+} ions as presented here, the values $\bar{\bar{d}} = 1.15$, 1.51, and 1.01 are estimated using Eq. (2) for Co^{2+}, Yb^{3+}, and Nd^{3+} ions, respectively. Since small doping concentrations of the ions in the samples does not modify the nature of the P4VP matrix significantly, one expects to obtain the same value for $\bar{\bar{d}}$ for the three samples. Hence, the above differences in the $\bar{\bar{d}}$ values must be ascribed to variations due to experimental errors, which manifest due to measurements being difficult. Thus, on the average, $\bar{\bar{d}} = 1.22 \pm 0.21$, somewhat different from the value $\bar{\bar{d}} = 1.33$ calculated for a percolating network. (It is noted that the P4VP network may not be an ideally percolating network.) Using this $\bar{\bar{d}}$ value, the n value for P4VP is calculated from Eq. (2) to be, on the average, 4.15 ± 0.90, in the temperature range 12.3 ± 0.7 K to 19.0 ± 1.0 K.

In order to ensure that localization, a condition for the occurrence of spin-fracton relaxation, is in existence the Ioffe-Regel criterion [5,17] must be satisfied

$$\lambda < \xi, \tag{3}$$

where λ and ξ denote, respectively, the fracton (or phonon) wavelength, and the characteristic length scale. Further, Eq. (3) implies that spin-fracton relaxation is effective at temperatures $T > T_L$ [17], where

$$T_L = (h/k)(v/\xi). \tag{4}$$

In Eq. (4), T_L, h, k, and v are, respectively, localization temperature, Planck's and Boltzmann's constants and the velocity of sound in the sample. As for v, its value can be calculated from those listed by Graebner et $al.$ [18] for a series of amorphous samples. For a polymer, an average of these values, 1.72×10^5 cm/s, can then be used. In order to estimate ξ, Chachaty et $al.$ [12] have shown that P4VP possesses a porous structure in which there exists a distribution of diameter of pores ranging from 3 nm to 50 μm. These pores are separated from each other by a region of relatively dense cross-linked P4VP polymer of width ~ 4 nm. To estimate the localization temperature, a self-similarity unit can then be considered to be constituted by the region covered by a dense polymer (4 nm) along with a pore of the minimum diameter (3 nm). The characteristic length scale can then be reasonably assumed to be $\xi = 7$ nm, in good agreement with the values listed in Ref. [18] for polymers. By substituting the values of ξ and v deduced here, one obtains $T_L = 11.8$ K from Eq. (4), lying eminently within the range of T_L values listed by Graebner et $al.$ [18] in several amorphous systems ($8 < T_L < 22$ K). Further, this temperature is very close to the average value of 12.3 ± 0.7 K obtained here for the onset of the $T^{4.16}$ dependence as the temperature increases.

It has been reported [1,19] that fractons can exist only in narrow temperature ranges. At lower temperatures, extended phonons become predominant, while particles modes appear at higher temperatures. The experimental data obtained here, limited to the upper limit of about 20 K, do not enable one to estimate a precise value for the higher end of the temperature range for observation of fractons in P4VP. However, n begins to decrease at 19 and 18 K in samples doped with $CoCl_2$ and $YbCl_3$, respectively. This indicates that the temperature range for the observation of fractons in P4VP is here limited to about 19 K.

Another criterion for the existence of spin-fracton relaxation is the nonexponential rise of magnetization, which cannot be verified by the plot of $S(\Omega)$ in the "modulation" method (Sec. I), which is the Laplace transform of the evolution of the EPR signal, due to the exchange interaction rendering such rise to become exponential [3,4,10,20] in the more concentrated sample with 2 wt % of $CoCl_2$ or, due to difficulty in precisely analyzing $S(\Omega)$ in the relatively weakly doped samples with 0.8 wt % of $NdCl_3$ and 0.5 wt % of $YbCl_3$, due to weak signals. Electron spin echo (ESE) and saturation recovery techniques are not feasible here due to relaxation times being too small. Fortunately, a nonexponential evolution of magnetization has, indeed, been established by NMR measurements on P4VP by Chachaty et $al.$ [12].

Finally, the existence of two well-known relaxation mechanisms, i.e., those effected by extended and localized phonons, is ruled out in P4VP because (i) the samples are in fractal state, and (ii) the dependency $T_1^{-1} \propto T^6$ due to extended phonons as observed in mineral glasses [21,22] is not observed here.

The relaxation data presented here on the Co^{2+}, Yb^{3+}, Nd^{3+} ions, possessing large spin-orbit couplings, in P4VP above 12.3 K are consistent with spin-fracton relaxation due to the following: (a) the matrix of P4VP possesses fractal nature; (b) the fulfillment of the Ioffe-Regel criterion in P4VP, indicating that (strong) localization is effective at $T > 12$ K; (c) the spin-fracton relaxation characterized by the fracton dimensionality $\bar{\bar{d}} = 1.22 \pm 0.21$ has here been clearly established; (d) a nonexponential rise in the relaxation rate in P4VP as verified by NMR measurements. They are described satisfactorily by the spin-fracton relaxation theories of Alexander, Entin-Wohlman, and Orbach [2,4,23]. In closing, it is noted that the verification of these theories has, indeed, been possible thanks to the "modulation" method, capable of measuring very fast relaxation rates.

[1] R. Vacher and E. Courtens, in *Phonons 89: Proceedings of the International Conference on Phonon Physics, Heidelberg, 1989* (World Scientific, Singapore, 1990).

[2] S. Alexander, O. Entin-Wholman, and R. Orbach, Phys. Rev. B **32**, 6447 (1985).

[3] S. Alexander, O. Entin-Wholman, and R. Orbach, Phys. Rev. B **33**, 3935 (1986).

[4] S. Alexander, O. Entin-Wholman, and R. Orbach, Phys. Rev. B **35**, 1166 (1987).

[5] According to R. Orbach, S. Alexander, and O. Entin-Wholman, in lecture notes, Summer School, University of California, Berkeley, 1989, two types of localization must be considered: "strong localization" due to geometrical factors (fractal structure), and "weak localization" produced by impurity scatterings, such as that in heme protein (Ref. [4]). The results presented here involve strong localization. (See also Refs. [2,3].)

[6] J. Szeftel and H. Alloul, Phys. Rev. Lett. **34**, 657 (1975); J. Non-Cryst. Solids **29**, 253 (1978).

[7] M. K. Bowman and L. Kevan, J. Phys. Chem. **81**, 456 (1977).

[8] S. R. Kurtz and H. J. Stapleton, Phys. Rev. B **22**, 2195 (1980).

[9] W. A. Philips, J. Low Temp. Phys. **7**, 351 (1972).

[10] H. J. Stapleton, J. P. Allen, C. P. Flyn, D. G. Stinson, and S. R. Kurtz, Phys. Rev. Lett. **45**, 1456 (1980).

[11] This is, however, not a sufficient condition. See J. Pescia, S. K. Misra, M. Zaripov, and Y. Servant, Phys. Rev. B (to be published), reporting spin-lattice relaxation of the ions Gd^{3+}, Mn^{2+}, Cu^{2+}, and Cr^{3+} possessing weak spin-orbit coupling, in P4VP. In these cases the relaxation was *not* spin fracton despite the fractal character of P4VP.

[12] C. Chachaty, J. P. Korb, J. R. C. Van Der Marel, W. Bras, and P. Quinn, Phys. Rev. B **44**, 4778 (1991).

[13] J. Pescia, Ann. Phys. (Paris) **10**, 389 (1965).

[14] G. Ablart and J. Pescia, Phys. Rev. B **22**, 1150 (1980).

[15] A statistical analysis of the fits revealed that they were indeed "good," as judged by the value of R^2, defined in the caption of Fig. 1. To this end, we are grateful to Professor Y. Chaubey of Concordia University (Department of Mathematics and Statistics).

[16] S. K. Misra, Phys. Rev. B **58**, 14 971 (1998).

[17] A. L. Ioffe and A. R. Regel, Prog. Semicond. **4**, 237 (1960).

[18] J. E. Graebner, B. Golding, and L. C. Allen, Phys. Rev. B **34**, 5696 (1986).

[19] E. Courtens, R. Vacher, and J. Pellous, NATO workshop "Fractals" (1989).

[20] P. Lopez and J. Pescia, Phys. Lett. **38A**, 109 (1972).

[21] S. B. Stevens and H. J. Stapleton, Phys. Rev. B **42**, 9794 (1990).

[22] D. Vergnoux, P. K. Zinsou, M. Zaripov, G. Ablart, J. Pescia, S. K. Misra, R. Rakhmatullin, and S. Orlinskii, Appl. Magn. Reson. **11**, 487 (1996).

[23] S. Alexander, C. Laermans, R. Orbach, and H. M. Rosenberg, Phys. Rev. B **28**, 4615 (1983).