Spin-lattice relaxation in the polymer resin poly-4-vinylpyridine doped with transition ions Cu^{2+}, Cr^{3+}, Mn^{2+}, and Gd^{3+} possessing weak spin-orbit coupling

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The temperature dependency of the spin-lattice relaxation rate (T_1^{-1}) in poly-4-vinylpyridine (P4VP) resin samples doped with 0.5–5.0 % weight concentrations of ions characterized by weak spin-orbit coupling, Cu^{2+}, Cr^{3+}, Mn^{2+}, and Gd^{3+} was investigated over the range 4.2–250 K. It was found to be quadratic and linear at very low and intermediate temperatures, respectively, well accounted for by the exchange interaction between ions modulated by lattice vibrations, the ions being distributed uniformly over the sample. At higher temperatures, and with a concentration of up to 3%, the relaxation rate became almost independent of temperature, described well by cross relaxation between exchange-coupled pairs of spins and individual spins. At concentrations higher than 3%, the Bloembergen-Wang three-reservoir model was found to account for the data satisfactorily at all temperatures. [S0163-1829(99)01614-8]

I. INTRODUCTION

While spin-lattice relaxation in ionic crystals may be considered to be well understood today,[1–4] the same is not true of amorphous materials, on which very few experimental data have been reported to date. This is due to their rather short relaxation times, making them difficult to be measured by conventional techniques, as well as to their complex nature due to microscopic disorder within them. The published results have been mainly confined to irradiated samples,[5–8] and doped glasses.[9–11]

The measurements carried out on amorphous samples, have shown that the temperature dependency of their relaxation rate, $T_1^{-1}(T)$, where T_1 is the relaxation time, is very different[5–8] from that observed in ionic crystals. In irradiated samples doped with very small concentrations of paramagnetic ions, the quadratic temperature dependency at very low temperatures changes to a linear dependency at intermediate temperatures. These results were satisfactorily explained by the mechanism of modulation of electron-nuclear or Fermi-contact hyperfine interaction between spins and two-level tunneling states (TLS) centers subjected to the tunneling effect in double-potential wells.

Faster dependency of relaxation rates, different from those in ionic crystals, have been reported in the literature. Stapleton *et al.*[12] found a $T^{6.6}$ dependency in biomolecular fractal structure. Stevens and Stapleton[9] and Vergnoux *et al.*[10] reported a T^6 dependency in mineral glasses doped with Yb^{3+} ions, which was ascribed to spin-phonon relax-

ation with a low effective Debye temperature, indicating that only the low-frequency phonons in the phonon spectrum (<1 THz) are instrumental in relaxing spins. On the other hand, Waplak *et al.*[13] observed a $T^{2.47}$ dependency at temperatures above 120 K for non-Kramers ions in a spin glass, which was attributed to spin-fraction coupling.

As for polymers, very few results have been reported.[7,8,14,15] These are mostly on irradiated samples, except for a recent publication,[16] dealing with a polymer doped with transition ions. It is worthwhile to study spin-lattice relaxation in polymers as these materials are of current interest. Chachaty *et al.*[16] showed that poly-4-vinyl-pyridene (P4VP) is an appropriate system well suited for doping by rare-earth and iron-group ions. In view of this, measurements of spin-lattice relaxation times T_1 were here carried out over an extended temperature range on this material, doped with weight concentrations between 0.5 and 5.0 % of the Cu^{2+}, Mn^{2+}, Cr^{3+}, and Gd^{3+} ions possessing very weak spin-orbit couplings, as a result of their orbital angular momentum being partially or completely quenched. Chachaty *et al.*[16] determined that P4VP possesses a fractal structure. (A study of P4VP samples doped by the Kramers ions Co^{2+}, Nd^{3+}, and Yb^{3+} characterized by strong spin-orbit coupling leading to the possibility of spin-fracton relaxation will be presented in a forthcoming paper.)

Spin-lattice relaxation times observed for all the four above-mentioned ions are sufficiently small, not amenable to be measured by conventional techniques such as saturation recovery or pulsed EPR (electron-spin echo). In order to measure very small relaxation times and to extrapolate them
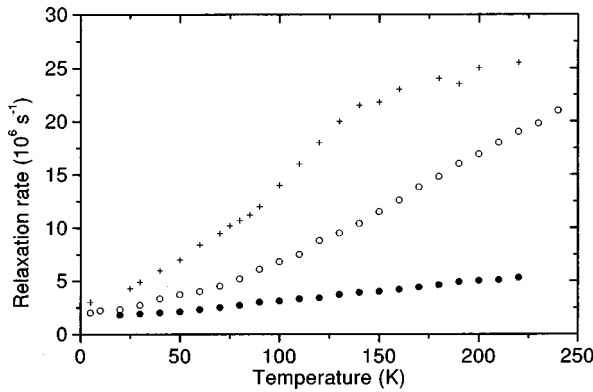
FIG. 1. Variation of the relaxation rate with temperature in the P4VP samples doped with $CuCl_2$ with weight concentrations: ($\bullet$) 1%; ($\bigcirc$) 2.8%; ($+$) 4.0%.

over an extended temperature range, the ''modulation'' technique using an amplitude-modulated microwave field was here used, the underlying principle is described in Sec. II. In order to attain sufficient precision, it is necessary that the signals are not too weak. Experimental results and their discussions are given in Sec. III. Conclusions are summarized in Sec. IV.

II. MODULATION METHOD TO MEASURE SPIN-LATTICE RELAXATION TIME

Measurements of relaxation times (T_1) were performed at the X band (8.9 GHz) over the temperature range 5–250 K by the modulation method,[17–19] in which the microwave field is amplitude modulated at a frequency f. An EPR signal (S) proportional to dM_z/dt, where M_z is the component of the magnetization along the external field, is detected in a pickup coil situated close to the sample and coaxial with the magnetic field. The relaxation time is estimated from the plot of S versus Ω ($=2\pi f$) by exploiting the relation $S=\Omega T_1/(1+\Omega^2 T_1^2)^{1/2}$.

III. EXPERIMENTAL RESULTS AND INTERPRETATION

The temperature dependences[20] of the observed relaxation rates, T_1^{-1}, for the P4VP samples doped with 1.0, 2.8, and 4.0 wt. % of $CuCl_2$ are shown in Fig. 1, while in Fig. 2 are displayed the relaxation rates observed for the P4VP samples doped with 5.0 wt. % of $CrCl_3$, 1.5 wt. % of $MnCl_2$, and 1.0 wt. % of $GdCl_3$. The features of these two figures can be represented by the general shape exhibited in Fig. 3. For some ions, the data correspond to only a few parts of this curve. (i) The linear part (region 1) is exhibited by all ions. (ii) All samples, except those doped with 1% of Gd^{3+}, or Cu^{2+}, exhibit the quadratic part (Fig. 3, region 2); this limitation is due to the measuring technique not being capable of measuring $T_1>10^{-6}$ s.

A. Spin-lattice relaxation effected by exchange interaction

Quadratic and linear temperature dependences were exhibited by irradiated frozen solutions of ethanol between 6 and 100 K as reported by Bowman and Kevan,[5] who proposed a model based on modulation of electron-nuclear di-
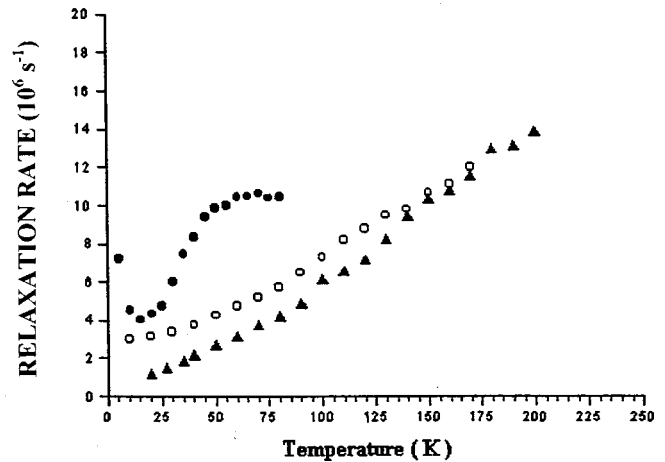

FIG. 2. Variation of the relaxation rate with temperature in the P4VP samples doped with weight concentrations: ($\bullet$) 5% of $CrCl_3$; ($\bigcirc$) 1.5% of $MnCl_2$; ($\blacktriangle$) 1.0% of $GdCl_3$.

polar interaction by phonons in the presence of TLS (two-level tunneling states) centers.[21,22] The latter are particles, which experience tunneling effect in double-potential wells. Accordingly, the expression for the relaxation rate is

$$T_1^{-1}=T^{1+\gamma}, \quad \text{where} \quad 0<\gamma<1, \tag{1}$$

which approximates to $T_1^{-1}\propto T$ at intermediate temperatures.

In irradiated β alumina, containing the cations Li, Na, or K, Kurtz and Stapleton[6] observed similar variations:

$$T_1^{-1}\propto T^n, \tag{2}$$

where, $2<n<4$ and $n=1$ at low and intermediate temperatures, respectively. They explained their data on the basis of modulation of Fermi-contact hyperfine interactions by phonons, where the TLS centers are the nuclei of Li, Na, or K.

These two models do not explain the data on polymers studied here because of the fact that at a given temperature
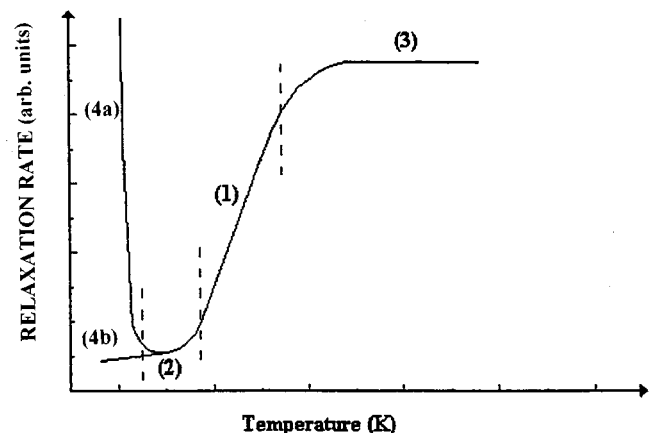

FIG. 3. General shape of experimental plots $T_1^{-1}(T)$ for the various samples doped with ions possessing weak spin-orbit couplings.

for small concentrations of paramagnetic ions the relaxation rates are 14 000 to 40 000 times faster[23–25] than those reported above.[5,6] This points to the need to look for a new relaxation mechanism, which turns out to be the exchange interaction between individual ions, as proposed recently.[23–25] The pertinent details are described below.

Taking into account the modulation of the exchange coupling between individual spins by lattice vibrations (phonons) in an amorphous material, assuming uniform distribution of spins in the sample, based upon standard theories of spin-lattice relaxation,[26] it was shown in Ref. 23 that the relaxation rate was proportional to λ^2 and v^{-5}, where λ is the spin-orbit coupling constant of the paramagnetic ion and v is the velocity of sound in the sample, and, most importantly, it is proportional to an integral that depends on temperature as follows:

$$I_{\text{EX}} = \frac{4\pi}{\xi^3} \int_0^{J_0} \frac{[J \ln(J/J_0)]^2 dJ}{\{\exp(J/kT) - 1\}}, \tag{3}$$

where $J = J_0 \exp(-\xi r)$ expresses the dependency of the exchange interaction upon distance r. By numerical evaluation of the above integral, it was shown in Ref. 23 that the temperature dependency, T^n, of the relaxation rate is characterized by the value $n \sim 2$ for $J_0 \sim 10$ K at very low temperatures, below about 10 K. On the other hand, it is easily seen that at intermediate temperatures the integral given by Eq. (3) leads to a linear dependency of the relaxation rate upon temperature. Accordingly, the T and T^2 dependences (Fig. 3, regions 1 and 2) are explained well by the mechanism of exchange interaction.

Further, the expression for the relaxation rate at high temperatures for the majority of mechanisms depends on the fifth power of the velocity of sound v in the sample, that is upon v^{-5}.[1,2,5,6] It is, therefore, necessary to ensure that the difference in the order of magnitude of the relaxation rate observed in irradiated samples and those presented here is not solely due to the difference in the respective velocities of sound. For a large number of amorphous samples,[27] one finds $1.19 \times 10^5 \text{ cm}^{-1} < v < 4.1 \times 10^5 \text{ cm}^{-1}$. The fifth power of the ratio 3.45 between the two limits leads to the factor 488 for the relaxation rates for the various systems, indisputably smaller than the ratio 14 000 to 40 000 between the measured relaxation rates at a given temperature as reported in Refs. 5 and 6 and those presented here. The relaxation mechanisms are, therefore, quite different, as confirmed further by the dependency of T_1^{-1} upon concentration in the cases considered here and its independence in the other cases.

B. Cross relaxation

For the case when the concentration of spins is rather large, cross relaxation between exchange-coupled pairs and individual spins becomes important at higher temperatures. Two cases are possible:

(i) *When there exists strong cross relaxation and weak spin-lattice relaxation of individual ions and exchange-coupled pairs:*[28]

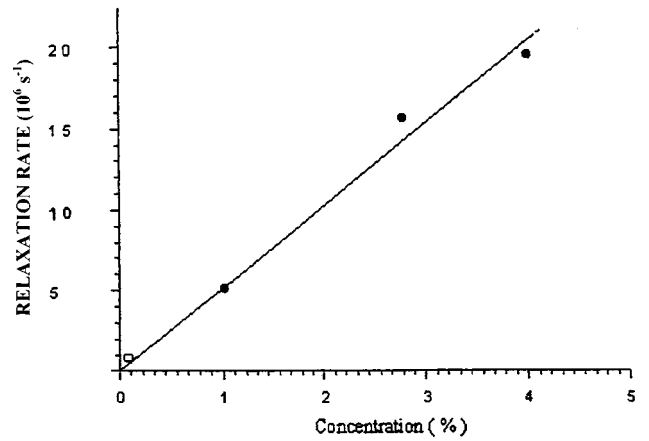$$T_1^{-1} \propto C\Delta'^3/\sinh(\Delta'/kT), \tag{4}$$

FIG. 4. Dependency of the spin-lattice relaxation rate upon concentration of the polymer sample P4VP doped with Cu^{2+} ions at 200 K. The solid circles represent the data presented here, while the empty circles are those of Chachaty *et al.* (Ref. 16).

where Δ' denotes the energy separation between the ground-state singlet and the triplet of an exchange-coupled pair, and C is the concentration of paramagnetic ions. It is seen from Eq. (4) that the relaxation rate depends linearly upon concentration. Combining the NMR results[19] with those presented here, it is seen from Fig. 4 that at 200 K the relaxation rate varies linearly with concentration of paramagnetic ions in the 0.1–4.0 % range, in accordance with Eq. (4). The effectiveness of the relaxation mechanism due to cross relaxations in the samples studied here is confirmed well by the excellent agreement shown in Fig. 5 between the data points for the samples doped with 1.5 wt. % of $MnCl_2$ as functions of temperature.

(ii) *When there exists very strong spin-lattice relaxation of excited pairs, much more predominant than cross relaxations:*[26]

$$T_1^{-1} \propto C^2 [1 + \exp(\Delta'/kT)]^{-1}. \tag{5}$$

For concentrations higher than 3%, the temperature dependency of the relaxation rate becomes weaker at higher tem-
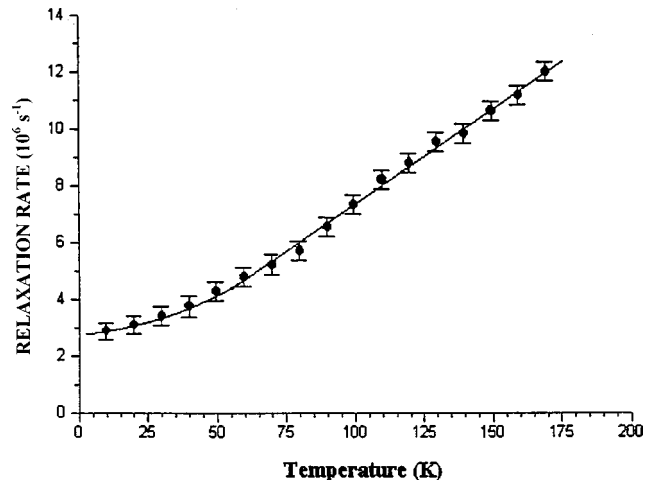

FIG. 5. Agreement of the experimental data versus concentration with Eq. (4) predicting linear dependence of the relaxation rate upon concentration for the P4VP sample doped with 1.5% of Mn^{2+}.
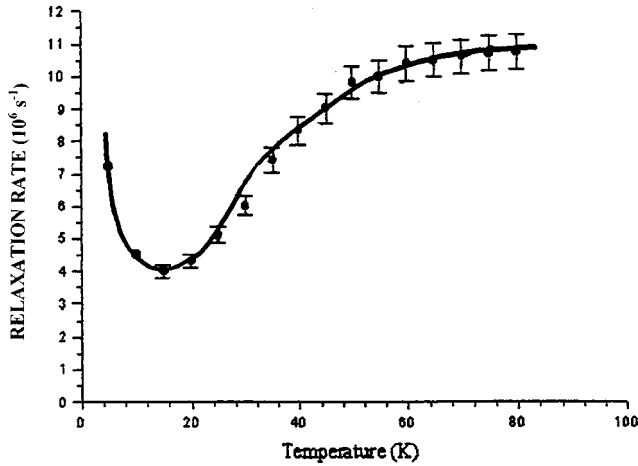
FIG. 6. Dependency ($\bullet$) of the relaxation rate (T_1^{-1}) upon temperature of a P4VP sample doped by 5% Cr^{3+} ions. The continuous line represents the plot of Eq. (6). T_{1ZE} appearing in Eq. (6), is calculated by Eq. (7) with $q = 0.28$.

peratures. Region 3 of Fig. 3 describing data at high temperatures is explained well by Eq. (5) which takes into account predominance of relaxation of exchange-coupled pairs, whose number increases with temperature, over exchange interaction between two ions which does not depend on this number.

C. Bloembergen-Wang model: highly concentrated samples

This model explains spin-lattice relaxation in samples highly concentrated in paramagnetic ions, which applies specifically to the samples doped with 5% of $CrCl_3$ and 4% of $CuCl_2$ studied here. The data on the sample doped with 5% of $CrCl_3$ are exhibited in Fig. 6. Taking into account the enhanced importance of exchange reservoir at such concentrations, the three-reservoir model of Bloembergen and Wang,[29] consisting of reservoirs of Zeeman exchange and lattice, appears to be specifically suited to describe these cases. In this model, the relaxation time can be described as

$$T_1(T) = T_{1Ze} + (\omega_z / \omega_{ex})^2 T_{1el} \qquad (6)$$

where T_{1Ze} and T_{1el} are Zeeman-exchange and exchange-lattice relaxation times and ω_z and ω_{ex} are Zeeman and exchange frequencies. T_{1el}, which represents the exchange-lattice coupling, varies with temperature due to phonons. It increases with decreasing temperature, becoming important only at low temperatures. Logically, $T_{1el} \propto 1/T^2$ for amorphous systems at low temperatures. On the other hand, T_{1Ze} does not depend on the lattice or phonons. As the temperature decreases, it increases, approaching infinity at Néel temperature, T_N. In this case, the expression suggested by Huber[30] can be used to describe it:

$$T_{1Ze} \propto 1/(T_N - T)^q, \qquad (7)$$

where $q = 0.28$.

According to Fig. 6, for the P4VP sample doped with 5% of Cr^{3+}, excellent agreement is found between the curve exhibiting Eq. (6), with T_{1Ze} and T_{1el} as described above,

and the data presented here. A similar excellent agreement is found for the sample doped with 4% Cu^{2+}. Equation (6) explains well the behaviors at high temperatures (region 3) and at low temperatures (region 4) as displayed in Fig. 3, which also includes the approach to Néel temperature. The latter is only observed when the exchange interaction is sufficiently strong to raise the Néel temperature above the lowest temperature achieved by the spectrometer. Magnetic susceptibility measurements on a P4VP sample doped with 5% of Cr_2O_3 confirm the existence of a strong exchange interaction. On the other hand, region 4b (Fig. 3), is exhibited by samples characterized by a sufficiently weak exchange interaction so that T_N is almost 0 K.

IV. CONCLUSIONS

The salient features of the study of relaxation rate presented here on amorphous cross-linked polymers (P4VP), doped by iron-group ions Cu^{2+}, Cr^{3+}, Mn^{2+}, and the rare-earth ion Gd^{3+} characterized by very weak spin-orbit coupling, with weight concentrations between 0.5 and 5%, are as follows.

(i) In samples with smaller concentration of paramagnetic ions, the spin-lattice relaxation rate, T_1^{-1}, exhibits a quadratic temperature dependency at low temperatures, which becomes linear at intermediate temperatures. These dependences have here been explained on the basis of exchange interaction between individual ions.

(ii) The relaxation rate varies linearly with concentration when it is less than 3%.

(iii) At higher temperatures, for strong concentrations of paramagnetic ions, the temperature dependency of the relaxation rate slows down. This behavior is described well by the mechanism of cross relaxation[28] between exchange-coupled spin pairs and individual spins.

(iv) At low temperatures, for concentrations higher than 3%, a better description is obtained by the three-reservoir model of Bloembergen and Wang.[29]

Finally, it is noted that the results presented here report a detailed study of spin-lattice relaxation in P4VP resin samples doped by paramagnetic ions possessing weak spin-orbit coupling. Moreover, the data have here been helpful to carry out a comprehensive analysis of spin-lattice relaxation data over an extended temperature range and varying concentrations. A convincing explanation of the data on the basis of various proposed theoretical models has here been accomplished.

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