# Electron spin-lattice and phase relaxation in ytterbium-activated phosphate glasses

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(Submitted 13 January 1984)
Pis'ma Zh. Eksp. Teor. Fiz. **39**, No. 4, 155–157 (25 February 1984)

Preliminary experimental results are reported on the temperature and concentration dependence of the spin-lattice and phase relaxation times of heavy paramagnetic ions in disordered matrices. Experiments were carried out in phosphate glasses with an $Yb^{3+}$ impurity by the electron-spin-echo method.

Many materials of importance in advanced technology have disordered structures (examples are pyroceramics, piezoceramics, mixed crystals, and high-temperature glasses). Study of the microstructure of these media is of fundamental importance and is being carried out by a variety of methods, including the electron-spin-resonance method (primarily for radiation-induced paramagnetic centers). It is well known that the magnetic and relaxation properties of rare-earth ions are most sensitive to the local fields created by the ligands of their surroundings. The ESR spectra of these ions thus contain a wealth of information about the properties of the matrix. Attempts to extract this information from spectra obtained by steady-state ESR methods, however, run into severe difficulties[1] in the case of glassy media because of the pronounced inhomogeneous line broadening. Some progress in this field has recently been made by using a laser-polarimeter method to detect the ESR.[2]

In this letter we report the first use of the electron-spin-echo method to study the spin-lattice relaxation and phase relaxation of trivalent rare-earth ions ($RE^{3+}$) in high-temperature glasses. Experiments in this area may be pertinent to the derivation of a theory for relaxation phenomena and also to the physics of glass. Several phenomena of the echo type (the "dipole echo" and the "tunneling echo," for example) have recently been observed in glassy matrices.[3] However, there has been essentially no study of the electron spin echo of paramagnetic ions in these media.

The experiments were carried out on an electron-spin-echo spectrometer with an observation frequency $\nu \sim 9.4$ GHz and a time resolution of $10^{-7}$ s. The echo signals were formed by two rf pulses 50 ns long. We studied phosphate glasses of the composition 25 $La_2O_3$ + 75 $P_2O_5$ with an ytterbium impurity. The samples were synthesized from "especially pure" materials. The relative concentrations of $Yb^{3+}$ ions were $c = 0.0012$ (sample I), $c = 0.004$ (II), and $c = 0.012$ (III). Signals corresponding to the electron spin echo of $Yb^{3+}$ were reliably observed in samples I, II, and III at temperatures $T \simeq 1.5$–7 K. The ESR spectrum of $Yb^{3+}$ constructed from the echo signals is shown in Fig. 1. For all of the glasses studied the decay of the echo is modulated by the interaction of $Yb^{3+}$ with magnetic phosphorus nuclei. To identify the mechanism for the phase relaxation in the precession of the spins we studied the temperature and concentration dependence of the phase-relaxation time $T_M$ (Fig. 2). Taken together,

  

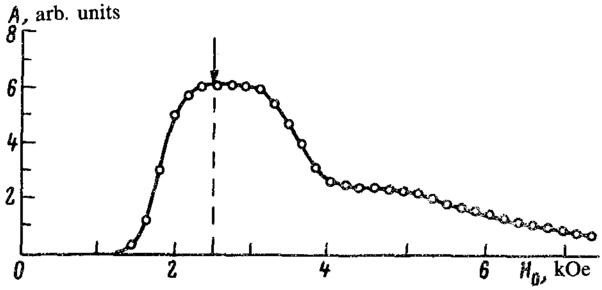


FIG. 1. The ESR spectra of $Yb^{3+}$ ions ($c = 0.0012$) in a phosphate glass at $T = 4.2$ K. A—Amplitude of the echo signal; arrow—the field $H_0$ at which the relaxation times were measured.

the experimental results suggest that the rate $T_M^{-1}$ is determined by a dipole-dipole interaction which is seen as a decay of the echo signal through the mechanism of a spectral diffusion caused by spin-lattice relaxation.[4]

The spin-lattice relaxation times $T_1$ were extracted from an analysis of the kinetics of the restoration of the echo signal after the imposition of a saturating pulse $\sim 1$ ms long. The $T_1^{-1}(T)$ dependence was studied for samples I, II, and III; some of the results are shown in Fig. 3. The $T_1^{-1}(T)$ dependence for sample I can be described well by the expression

$$T_1^{-1} = 60T + 10^{-3}T^9, \tag{1}$$

where the first term corresponds to the direct spin-lattice relaxation, and the second to a Raman process. Temperature-independent regions (plateaus) appear on the $T_1^{-1}(T)$

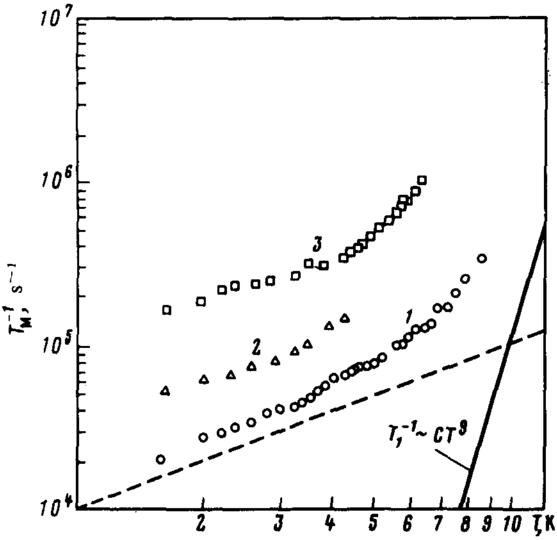


FIG. 2. Temperature dependence of the rate of the phase relaxation of $Yb^{3+}$ ions in phosphate glass samples. 1—Sample I; 2—II; 3—III; dashed line—the dependence $T_M^{-1} \sim T$.

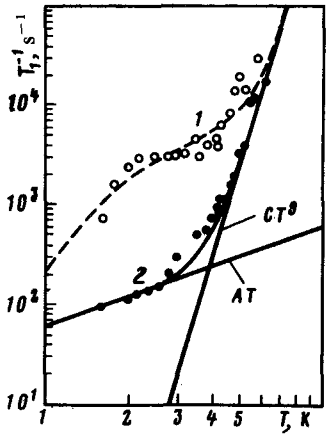


FIG. 3. Temperature dependence of the rate of the spin-lattice relaxation of $Yb^{3+}$ ions in phosphate glass samples. 1—Sample I; 2—III; solid line—expression (1); dashed curve—expression (1) with (2).

dependence as the $Yb^{3+}$ concentration is raised (samples II and III). We attribute these regions to a cross relaxation through a pair of $Yb^{3+}$ ions[5,6] in an excited state. These regions can be described satisfactorily by introducing another term

$$B[1 + \exp(\Delta/T)]^{-1} \tag{2}$$

in expression (1), where $B = B'C^2 = 3\times 10^3$ (sample II) or $2.1\times 10^4$ (III), and $\Delta \simeq 5$ K. It may be that the formation of such $Yb^{3+}$ pairs results from the properties of the basic microstructure of the phosphate glass.

In summary, the electron-spin-echo method is an effective tool for studying the structural, magnetic, and relaxation properties of $RE^{3+}$ ions in disordered media. Important information about the structure and properties of glasses can apparently be obtained by studying the electron spin echo of activator centers in the face of external agents (pressure, static and alternating electric fields, ultralow temperatures).

We thank S. G. Lunter for synthesizing the samples and V. S. Zapasskiĭ for constant interest in this study.


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Translated by Dave Parsons
Edited by S. J. Amoretty