Direct observation of the freezing-in of the spin-lattice relaxation of the electrons in small metallic particles

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(Submitted 12 February 1986)
Pis'ma Zh. Eksp. Teor. Fiz. **43**, No. 7, 337–338 (10 April 1986)

The results of the first experimental studies by the spin-echo method of the spin-lattice relaxation of electrons in small metallic particles (Li, Na, K, Mg, and Ag) are presented. The spin relaxation in the particles is found to be much slower than in the bulk metal.

The discrete nature of the energy levels of conduction electrons in small metallic particles, which results from the spatial limitation of the orbital motion of electrons, accounts for the appreciable difference between the electronic and magnetic properties of such particles and the properties of the bulk metal.[1,2] The quantization of the electronic levels in small particles of various metals was detected experimentally in the measurements of the heat capacity, static magnetic susceptibility, electron (stationary) resonance and nuclear magnetic resonance (see review articles in Ref. 3). In the present letter we report the use, for the first time, of the electron-spin-echo method to study the properties of the spin system of the conductivity electrons in small metallic particles. Our results show that the spin-lattice relaxation of electrons slows down appreciably as a result of electronic-level quantization and discrete nature of the phonon spectrum.

Th electron spin echo was measured with a relaxometer with a working frequency of $\sim$9.4 GHz and a time resolution of 5×10^{-7} s over a temperature range of 2 to 120 K. The behavior of the spin system was studied on the basis of the damping of a stimulated echo[4] and by the method of successive pulse trains.[5] We studied samples of small metallic particles obtained by two methods. The first method involved a joint deposition of a vaporizable metal (Li, Na, K, Mg) and a matrix gas (CO_2) onto a substrate cooled by liquid nitrogen. The particle sizes varied over a broad range from single atoms to $\sim$200 Å. To reduce the number of individual atoms and few-atom clusters, the samples were heat treated for one hour at a temperature of 190 K in inert atmosphere. The second method involved the use of a chemical reaction of silver nitrate with tannin and potash in a gelatin medium to produce colloidal silver particles in a gelatin matrix. Electron micrographs showed that the particle size varied within 30–50 Å.

Figure 1 shows the results of the measurement of the time dependence of the amplitude of a stimulated echo between the second and third probing pulses in Li, Na, K, Mg, and Ag particles. Figure 2 shows the change in the amplitude of the primary echo in silver particles as the repetition period of the pulse train is increased (the method of successive pulse trains). The measurements were carried out at different temperatures.

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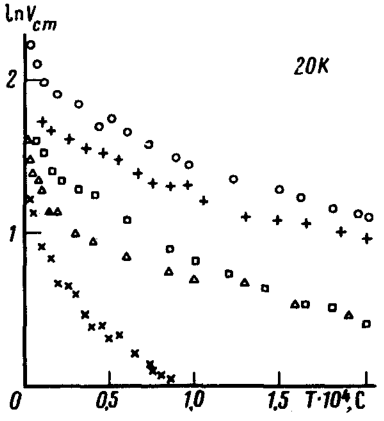

FIG. 1. Decay of the amplitude of a stimulated echo in the following particles: Li (O), Na (□), K (+), Mg (×), and Ag (Δ).

We see from the given plots that the kinetics of the spin relaxation in the test samples is essentially of a nonexponential nature and that the relaxation of the spin system occurs on a time scale much greater than that of the spin-lattice relaxation of the conduction electrons in bulk metals. At a temperature of 20 K, for example, we have $T_1 \sim 10^{-8}$ s in bulk potassium samples[6] and $T_1 \sim 10^{-9}$ s in silver samples.[7] The amplitude of the stimulated echo (Fig. 1) falls off much more rapidly than the change in the amplitude of the echo in the method of successive pulse trains (Fig. 2). This behavior is apparently attributable to the effect of spectral diffusion on the damping of the stimulated echo.

The average spacing between the electronic levels, Δ_e, and the minimum phonon energy, Δ_{ph}, for 30-Å silver particles are estimated to be

$$\Delta_e \sim E_F/N \sim 100\text{K} \quad \text{and} \quad \Delta_{ph} \sim \Theta_D/N^{1/3} \sim 30\,\text{K},$$

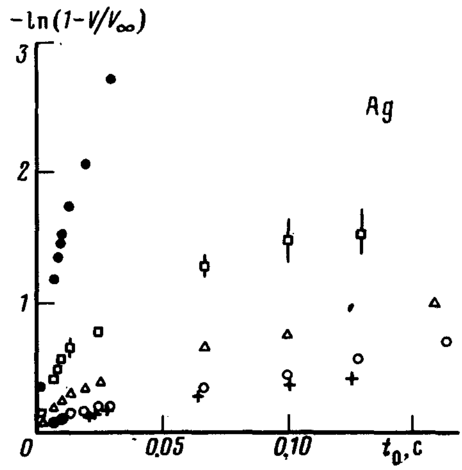

FIG. 2. The reduced amplitude of the primary echo V/V_∞ versus the repetition period of a train of probing pulses in silver particles at the following temperatures: 35 K (●), 20 K (□), 10 K (Δ), 4.2 K (O), and 2.0 K (+). $V = V(t_0)$ and $V_\infty = V(t_0) = \infty$.

where E_F is the Fermi energy, Θ_D is the Debye temperature, and N is the number of atoms in the particle. At $T \ll \Delta_e$ the spin-lattice relaxation must be completely blocked. However, since the metallic particles are in contact with the matrix, the relaxation may be caused by interaction of the conduction electrons with the charged or paramagnetic centers situated in the matrix or on the surface of the particles. The relaxation may also stem from the surface interaction of metallic particles with the thermal vibrations of the matrix. The nonexponential nature of the time dependence of the measured signals is attributed to the spread of the particles in size (and hence in Δ_e and T_1) and to the statistical distribution of the energy levels in particles of a given size.[1,2]

We wish to thank R. G. Mustafin for help with the measurements and I. A. Garifullin and V. A. Zhikharev for useful discussions of the results of this study.

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Translated by S. J. Amoretty