Manifestation of a tunneling effect in the electron spin resonance of small potassium particles

F. G. Cherkasov, A. Ya. Vitol, and M. F. Galyautdinov
Physicotechnical Institute, Kazan' Branch of the Academy of Sciences of the USSR

(Submitted 25 November 1988)
Pis'ma Zh. Eksp. Teor. Fiz. **49**, No. 1, 37–39 (10 January 1989)

Measurements of the electron spin resonance of small potassium particles reveal consequences of a quantum-size effect in the electron energy spectrum. They also reveal a temperature dependence of the width of the resonant line which is unusual for such particles. This temperature dependence is attributed to a tunneling of electrons between particles.

The electron energy spectrum has a discrete structure in sufficiently small metal particles. Manifestations of discrete electron energy levels in various magnetic effects have previously (Ref. 2, for example) been studied in systems with metal particles which do not interact with each other (which are electrically neutral[1]). In this letter we report the observation and study of an electron spin resonance (ESR) and the magnetic susceptibility in small potassium particles. The results show that the resonant properties of the metal are significantly influenced by not only the discrete nature of the electron levels but also tunneling transitions of electrons from one particle to another (after a thermal excitation of these electrons).

The ESR was studied at a frequency of 9.4 GHz over the temperature range 1.6–400 K. Particles of metallic potassium were produced inside KBr crystals by solid-phase electrolysis (followed by an annealing and a quenching in liquid nitrogen). An electrolytic (or additive) coloring of the crystals at 400–500 °C of this type led to the appearance of F centers, which, after reaching a certain concentration ($\gtrsim 10^{18}$ cm^{-3}), converted into colloidal metal particles with diameters less than 50 Å in the course of the annealing.[3,4] The samples were highly stable during the ESR measurements (6–8 h).

Figure 1 shows the magnetic susceptibility χ_s, which is proportional to the integral intensity of the ESR signal at various temperatures, as the relative quantity $\chi_s/\chi_e \sim f(T)$, where χ_e is the temperature-independent value of this susceptibility. It can be seen from Fig. 1, a and b, that at low temperatures the susceptibility has a Curie-like behavior $\chi \sim T^{-\alpha}$, where $\alpha = 0.75$. This behavior of $\chi(T)$ agrees qualitatively with the theoretical predictions[1,2] that the discrete nature of the electron levels will affect the paramagnetism of particles having an odd number of electrons. The observed deviation from the Curie law $\chi \sim T^{-1}$ (Fig. 1b) cannot be described satisfactorily in the theory of Refs. 1, 2, and 5, which incorporates a discrete structure of levels and an effect of spin-orbit coupling on $\chi(T)$ in particles. We believe that this aspect of $\chi(T)$ stems from an additional and effective interaction in the system (see the analysis of data on the ESR linewidth below). It can also be seen from Fig. 1b that the transition to a temperature-independent Pauli susceptibility occurs at $T_c = 140$ K. According to Refs. 2 and 5, we have $kT = \delta$ at this point, where δ is the average distance

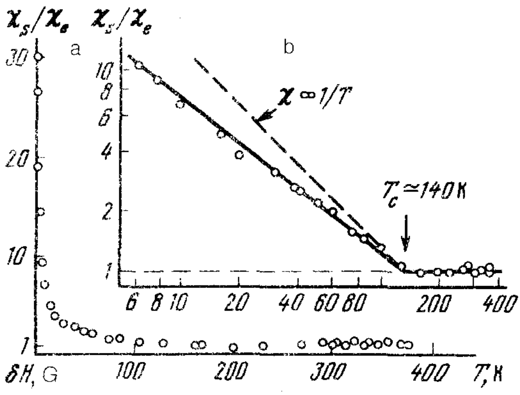

FIG. 1. Relative magnetic susceptibility χ_s/χ_e in small potassium particles versus the temperature. a—Linear scale; b—logarithmic scale.

between the electron levels in the particles. Using the relation[1] $\delta = 4E_F/3N$, where E_F is the Fermi energy, we find that the number of electrons in the particle is $N = 235$ for a given sample with $\delta = 0.012$ eV. This number corresponds to an average particle diameter $d = 32$ Å.

Figure 2 shows the temperature dependence of the linewidth $\delta H(T)$ for the same sample. We can draw the conclusion that a quantum-size effect involving the electron levels in the particles is influencing δH simply by comparing the data shown in this figure with the results of ESR measurements in bulk potassium (in which, at 77 K and 300 K, for example, the linewidths are 30 G and 125 G, respectively[6]). It follows from the theory of Refs. 1, 2, and 7 that the spin relaxation of electrons is frozen in particles having discrete level structure,[8] so a very small temperature-independent ESR linewidth would be expected. However, many studies[2] have shown that the observed ESR line in small particles is inhomogeneously broadened, primarily by the hyperfine interaction of electrons with nuclear spins.[9] For potassium particles with a diameter of 30–40 Å the hyperfine broadening amounts to[9] 6–9 G (see also the experimental data of Ref. 4), or an order of magnitude greater than the residual linewidth measured in our particles ($d = 32$ Å): $\delta H = 0.6$ G at low temperatures (Fig. 2). The absence of a hyperfine broadening of the resonance in our samples might be a consequence of a fairly strong exchange interaction between the electron spins in the different particles.

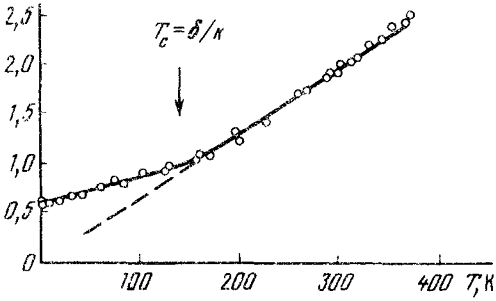

FIG. 2. Temperature dependence of the ESR linewidth in potassium particles with a diameter of 32 Å.

An experimental situation of this sort was predicted in Ref. 10 on the basis of a simple tunneling model which gives a satisfactory description of the narrowing of the ESR line. That model, however, fails to explain the linear dependence $\delta H(T)$ at high temperatures (Fig. 2). The mechanisms (phonon and surface mechanisms) for a spin relaxation of electrons in small particles which were recently proposed[11] fail to describe the behavior $\delta H(T)$, since in the absence of exchange those mechanisms would be masked by hyperfine broadening.[9]

Apparently the most appropriate mechanism for our case is the mechanism of thermally activated tunneling,[12,13] in which the charge carriers initially are excited thermally above an electrostatic potential barrier E_c and then tunnel from one neutral particle to another. The activation energy[13] $E_c \simeq e^2/Kd$ is ~ 600 K for particles with $d \simeq 32$ Å and $s \simeq 20$ Å, where $K = \epsilon(1 + d/2s)$, s is the distance between particles, calculated from the model of Ref. 10, and ϵ is the dielectric constant, ≈ 5 for KBr. The conditions for thermal excitation of electrons above E_c correspond to temperatures of 650–700 K, at which the potassium particles were produced in the KBr. We also assume that there are two spin subsystems in a sample, consisting of delocalized (tunneling) e electrons and localized s electrons, between which an exchange interaction with spin flip occurs. The behavior of the ESR in this case will depend on whether a combined resonance of the e and s electrons is realized (the bottleneck regime[14,15]). In our experiments, this regime could occur, since the measured shift of the g-factor differs by $\sim 10^{-4}$ from the value for a free electron, g_0. We thus have $g = g_s \cong g_0$. If the pumping of the rf energy to the matrix phonons (through the e electrons) occurs at a rate T_{eL}^{-1}, where $T_{eL}^{-1} \gtrsim T_{sL}^{-1}$, and T_{sL}^{-1} is the rate of spin-lattice relaxation in the particle itself, and if the rate of relaxation of the e electrons through exchange with s electrons satisfies $T_{es}^{-1} > T_{eL}^{-1}$, then the observed linewidth can be described as $\delta H \sim T_{es}^{-1}$. Using the balance equation $T_{se}/T_{es} = \chi_s/\chi_e$, we find

$$\delta H \propto \frac{1}{T_{se}} \frac{\chi_e}{\chi_s}, \tag{1}$$

where $T_{se}^{-1} = (4\pi/\hbar)(\rho J)^2 kT$ is the "Corringa" rate of the relaxation of s electrons due to the exchange interaction with e electrons,[15] ρ is the state density at the Fermi surface, and $J/\hbar$ is the exchange energy. Using (1) and the values $\rho = 33.2$ eV^{-1} (from the free-electron model) and $J = 7.3 \times 10^{-6}$ eV, we have generated a description of the functional dependence $\delta H(T)$ observed in the potassium particles (the solid line in Fig. 2). The values of χ_s/χ_e from Fig. 1a have been used.

We are indebted to G. B. Teĭtel'baum and G. G. Khaliullin for useful discussions.

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Translated by Dave Parsons