Theory of spin-lattice relaxation of conduction electrons in small metallic particles

G. G. Khaliullin and M. G. Khusainov

Physicotechnical Institute, Academy of Sciences of the USSR, Kazan

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A study is made of relaxation of the longitudinal spin magnetization of electrons in an ensemble of independent metal particles inside an insulating matrix. The particles are assumed to be so small that the electron spectrum becomes discrete and the distribution of levels is described by correlation functions introduced by Gor'kov and Éliashberg [Sov. Phys. JETP **21**, 940 (1965)]. Spin-orbit scattering of electrons by thermal lattice vibrations and by inhomogeneities of the potential near a boundary is considered. In the limit when the vibrations of metal and matrix atoms are not coupled, the two relaxation mechanisms are suppressed because of the discrete nature of the electron and phonon spectra. Spin reorientation by lattice vibrations is the result of renormalization of the phonon spectrum because of the coupling with the matrix, whereas relaxation due to static defects is the effect of broadening of electron levels because of the electron-phonon and Coulomb interactions. It is found that the decay of excitations is weak and a quasistatic description is valid. At low temperatures the rate of relaxation fluctuates strongly from particle to particle so that the time dependence of the total magnetization is nonexponential and is governed by the nature of the level statistics.

I. INTRODUCTION

The discrete and random nature of the spectrum of elementary excitations in small particles gives rise to significant differences of their physical properties from those of bulk samples.[1–3] The response of an ensemble of small metal particles to an external field is described statistically by introducing the average energy interval Δ and the distribution function $R(\omega)$ that governs the probability that two levels are separated by a spacing ω. According to Refs. 1 and 4, three types of level statistics may be encountered, depending on the strength of the spin-orbit interaction and on the magnetic field: orthogonal, symplectic, and unitary. All three types of distribution are characterized by level repulsion which is manifested by periodic oscillations of the function $R(\omega)$ if $\omega > \Delta$ and by decay in accordance with the power law $R(\omega) \propto \omega^n$ if $\omega < \Delta$. On the other hand, the available experimental data (Refs. 2 and 3) do not answer to the fundamental question whether such a correlation between levels exists or whether they are distributed at random $[R(\omega) = \text{const}]$, as assumed, for example, by Kubo.[5]

Clearly, the repulsion effect should be manifested above all when the response of electrons at frequencies $\omega \lesssim \Delta$ is important, because the oscillation amplitude $R(\omega)$ is very small if $\omega > \Delta$. We shall analyze one of these problems, the relaxation of the spin magnetization of conduction electrons. It is assumed that, as in the case of a bulk metal,[6,7] the main decay mechanism is the spin-orbit scattering by phonons and static defects. Since this results in transitions with an energy of the order of T, at temperatures $T < \Delta$ the rate of relaxation is very sensitive to the degree of correlation of the levels. Moreover, changes in the spin relaxation can give information on the nature of coupling of the metal atoms to the insulating medium, since it is the interaction with the medium (matrix) that results in some broadening of a discrete phonon spectrum of a small particle and is responsible for the nonzero spectral density of phonons at the frequency of electron transitions.

2. SPIN-ORBIT SCATTERING BY PHONONS

We shall consider first the process of relaxation of the longitudinal magnetization M_z in a single particle. In accordance with the theory of slightly nonequilibrium processes,[8] the decay $M_z(t)$ is exponential and the rate of relaxation can be described in terms of the imaginary part of the Fourier transform of a retarded Green function:

$$\tau_{sp}^{-1} = \lim_{\omega\to+0} \{\mathrm{Im}\langle\langle [S_z, H_{ep}] \,|\, [S_z, H_{ep}]\rangle\rangle_\omega / \chi\omega\}. \tag{1}$$

Here, S is the total electron spin and χ is the static spin susceptibility. The Hamiltonian of the electron-phonon interaction H_{ep} can be written in the form

$$H_{ep} = \sum_{\lambda,\lambda',\mathbf{q},\alpha,\beta} \langle\lambda\alpha|U_\mathbf{q}|\lambda'\beta\rangle a_{\lambda\alpha}^+ a_{\lambda'\beta}\varphi_\mathbf{q}, \tag{2}$$

where

$$U_\mathbf{q} = \left\{1 + \frac{\lambda_{so}}{\varepsilon_F}[\mathbf{n}\mathbf{n}']\mathbf{S}\right\} \frac{w}{u(NM)^{1/2}} e^{i\mathbf{q}\mathbf{r}};$$
$$\varphi_\mathbf{q} = (\omega_q/2)^{1/2}(b_\mathbf{q} + b_{-\mathbf{q}}^+);$$

$a_{\lambda\alpha}^+$ and $a_{\lambda\alpha}$ are the operators representing creation and annihilation of electrons in a state λ with a spin index α; $\varphi_\mathbf{q}$ is the operator of the field of phonons with a wave vector $\mathbf{q}$ and a frequency ω_q in a small particle. Moreover, λ_{so} is the spin-orbit interaction parameter; ε_F is the Fermi energy; w is the amplitude of the Coulomb potential of the lattice ions; N, M, and u are, respectively, the number of atoms, their mass, and the velocity of sound in a metallic particle; finally, $\mathbf{n}$ and $\mathbf{n}'$ are the directions of the electron momentum before and after the scattering, respectively.

Substituting Eq. (2) into Eq. (1) and then adopting the standard technique of the Green functions,[9] we find the spin-phonon relaxation rate τ_{sp}^{-1}:

$$\tau_{sp}{}^{-1}=4\Big[\sum_{\lambda}\mathrm{ch}^{-2}\Big(\frac{\xi_\lambda}{2T}\Big)\Big]^{-1}$$
$$\times\sum_{\mathbf{q},\lambda'>\lambda}\Big\{|\langle\lambda\uparrow|U_{\mathbf{q}}|\lambda'\downarrow\rangle|^2\,\mathrm{Im}\,D_q(\xi_{\lambda'}-\xi_\lambda)$$
$$\times\Big[\mathrm{ch}\frac{\xi_{\lambda'}}{2T}\,\mathrm{ch}\frac{\xi_\lambda}{2T}\,\mathrm{sh}\Big(\frac{\xi_{\lambda'}-\xi_\lambda}{2T}\Big)\Big]^{-1}\Big\}, \qquad (3)$$

where $D_q(\omega)$ is the retarded Green function of phonons in a small particle and ξ_λ is the energy measured from the chemical potential. Moreover, allowance is made in Eq. (3) for the fact that

$$\chi=\int_0^{1/T}d\tau\langle S_zS_z(i\tau)\rangle=\frac{1}{8T}\sum_{\lambda}\mathrm{ch}^{-2}\Big(\frac{\xi_\lambda}{2T}\Big). \qquad (4)$$

The square of the matrix element in Eq. (3) can be written as follows:

$$|\langle\lambda\uparrow|U_{\mathbf{q}}|\lambda'\downarrow\rangle|^2$$
$$=\frac{1}{9}\Big(\frac{\lambda_{so}}{\varepsilon_F}\Big)^2\frac{w^2}{NMu^2}\,|\langle\lambda|e^{i\mathbf{qr}}|\lambda'\rangle|^2\Big[(qa)^2+\Big(\frac{a}{d}\Big)^2\Big]. \qquad (5)$$

Here, a is the lattice constant and d is the diameter of a small particle. An additional factor in the square brackets is associated with the following circumstance. Since the states $|\lambda\alpha\rangle$ are already affected by the periodic spin-orbit potential of the lattice, spin flip is also due to the first term in the operator $U_{\mathbf{q}}$ of Eq. (2). Yafet[7] demonstrated that this contribution compensates for the matrix element of the second part of $U_{\mathbf{q}}$ of Eq. (2) to within terms linear in (qa). This compensation occurs only for crystals with a center of inversion, because otherwise (qa) changes to the relative role of the crystal potential, which is odd with respect of the coordinates under inversion conditions. In our case the potential of the atoms within the volume of a small particle has central symmetry, whereas the potential of the surface layer with a relative weight (a/d) does not have such symmetry.

An estimate of the square of the matrix element in Eq. (5), by a semiclassical method,[10,1] gives

$$|\langle\lambda|e^{i\mathbf{qr}}|\lambda'\rangle|^2\approx\begin{cases}2(q/p_F)^2, & qd<1\\ (a/d)^3p_F/\pi q, & qd>1\end{cases}. \qquad (6)$$

In further calculation of the rate of relaxation in accordance with Eq. (3) it is necessary to know the phonon Green function $D_q(\omega)$. If the vibrations of atoms in a small particle and the surrounding medium are independent, the scattering of electrons by phonons is blocked because oscillations in a particle have a strictly discrete set of frequencies beginning from the minimum value $\omega_m=\pi u/d$. In reality, relaxation finally occurs because of the coupling at the metal-insulator interface. We shall consider two cases which represent limits of the strength of this coupling.

3. QUASICONTINUOUS PHONON SPECTRUM

If the interaction between the metal and matrix atoms is sufficiently strong, the effective spectrum of long-wavelength vibrations of such a coupled system becomes continuous and is characterized by a Debye frequency ω_D and the average density of the phonon states $N(\omega)$ is common to the whole heterogeneous system. Substituting now Eqs. (5) and (6) together with the quantity

$$\mathrm{Im}\,D_q(\omega)=\frac{\pi\omega_q}{2}[\delta(\omega-\omega_q)-\delta(\omega+\omega_q)] \qquad (7)$$

into Eq. (3) and then integrating with respect to the phonon frequency $\omega_q=uq$, we obtain

$$\tau_{sp}{}^{-1}=A\Big[\sum_{\lambda}\mathrm{ch}^{-2}\Big(\frac{\xi_\lambda}{2T}\Big)\Big]^{-1}$$
$$\times\sum_{\lambda'>\lambda}\Big\{\Big(\frac{\xi_{\lambda'}-\xi_\lambda}{2T}\Big)^{\alpha}\Big/\mathrm{ch}\frac{\xi_{\lambda'}}{2T}\,\mathrm{ch}\frac{\xi_\lambda}{2T}\,\mathrm{sh}\Big(\frac{\xi_{\lambda'}-\xi_\lambda}{2T}\Big)\Big\}. \qquad (8)$$

The values of the relaxation parameter A and of the exponent α in Eq. (8) depend on the ratio of the frequency of the electron transition and the characteristic frequency $\omega_m=\pi u/d$:

$$A=\frac{2}{15\pi}\frac{1}{T_{sp}}\frac{\Delta}{\omega_m}, \qquad \alpha=5 \qquad (9)$$

if $\xi_{\lambda'}-\xi_\lambda<\omega_m$, or

$$A=\frac{1}{15}\frac{1}{T_{sp}}\frac{\Delta}{2T}, \qquad \alpha=4 \qquad (10)$$

if $\omega_D>\xi_{\lambda'}-\xi_\lambda>\omega_m$. Here, $\Delta=4\varepsilon_F/3N$ and the rate of longitudinal relaxation in a bulk metal is

$$\frac{1}{T_{sp}}=\frac{5\pi^4}{24}\Big(\frac{\lambda_{so}}{\varepsilon_F}\Big)^2\frac{w^2}{Mu^2}\Big(\frac{2T}{\omega_D}\Big)^4\frac{2T}{\varepsilon_F}. \qquad (11)$$

Both the relaxation rate τ_{sp}^{-1} of Eq. (8) and the magnetization amplitude $M_z(0)\propto\chi$ are governed by details of the electron spectrum and fluctuate from particle to particle. The time dependence of the magnetization of the ensemble of the particles can be obtained by averaging the expression

$$M_z(t)=M_z(0)\exp(-t/\tau_{sp}) \qquad (12)$$

over all the realizations of the random spectrum.

a) Low temperatures, $T<\Delta$. In this case the main contribution to Eqs. (4) and (8) comes from two states λ and λ' closest to the Fermi level. If the chemical potential is defined on the basis of conservation of the number of quasiparticles in the odd occupancy case

$$\mathrm{th}\frac{\xi_{\lambda'}}{2T}+\mathrm{th}\frac{\xi_\lambda}{2T}=1,$$

we find instead of Eq. (8) that

$$\tau_{sp}{}^{-1}(\omega)=Af_\alpha\Big(\frac{\omega}{2T}\Big), \quad f_\alpha(x)=\frac{x^\alpha}{\mathrm{sh}\,x\,(4+\mathrm{sh}^2x)^{1/2}}, \qquad (13)$$

where $\omega=\xi_{\lambda'}-\xi_\lambda$. If the number of electrons in a particle is even, we have to substitute in Eq. (13) the quantity $f_\alpha(x)=x^\alpha/2\sinh x$. We shall consider the specific case of an ensemble of small particles with an odd number of electrons, since in the case when $T<\Delta$ it is the "odd" particles that govern the magnetization of the system (particularly in the case of light metals with a weak spin-orbit interaction[11]). We can easily show that the dependence of $M_z(0)$ on ω is weak and, for the sake of simplicity, we shall ignore it. Substituting Eq. (13) into Eq. (12) and averaging the latter over the probability $P(\omega)$ of a given spacing ω between the neighboring levels, we obtain

$$m(t)\equiv\langle M_z(t)/M_z(0)\rangle=\int_0^\infty d\omega\, P(\omega)\exp[-t/\tau_{sp}(\omega)]. \qquad (14)$$

It is shown in Refs. 1 and 4 that the electron spectra of metals with a weak, $\lambda_{so}^2<\varepsilon_F\Delta$, and strong spin-orbit coupling should be described respectively by the orthogonal and symplectic statistics with the following correlation functions for the neighboring levels (see Ref. 11):

$$P_{or}(\omega)=\frac{\pi\omega}{2\Delta^2}\exp\left(-\frac{\pi\omega^2}{4\Delta^2}\right),$$

$$P_s(\omega)=\left(\frac{8}{3\pi^{1/2}}\right)^6\frac{\omega^4}{\Delta^5}\exp\left[-\left(\frac{8\omega}{3\pi^{1/2}\Delta}\right)^2\right]. \qquad (15)$$

The repulsion between the levels is manifested more clearly in the case of a symplectic ensemble, since the spin-orbit interaction lifts additionally the level degeneracy. In the case of a random distribution of levels the probability is $P(\omega)=\Delta^{-1}\exp(-\omega/\Delta)$ (Ref. 5).

After short times $t<A^{-1}$ the reduced magnetization of Eq. (14) decays exponentially at an average rate

$$\langle\tau_{sp}^{-1}\rangle=A\int_0^\infty d\omega\, P(\omega)f_\alpha(\omega/2T). \qquad (16)$$

The characteristic energy scale is now $\omega\sim T<\Delta$ and, therefore, we can use Eq. (9) for A and α. [We shall consider the specific case when $(\Delta/\omega_m)\sim(\varepsilon_F/\omega_D)(a/d)^2\lesssim 1$.] Then, the relaxation rate $\langle\tau_{sp}^{-1}$ corresponding to the onset of decay of the magnetization behaves as follows:

$$T_{sp}^{-1}(2T/\omega_m)(2T/\Delta)^n\ll T_{sp}^{-1},$$

where $n=1$, 4, and 0, respectively for the three correlation functions given above.

If $tA>1$, the magnetization decays nonexponentially:

$$m(t)\approx 1-\int_0^{\omega^*} d\omega\, P(\omega),$$

$$\omega^*\approx T\ln\{4At[(\ln 4At+\alpha)/2]^\alpha\}. \qquad (17)$$

If there is no correlation between the levels $\ln m(t)\sim-\omega^*/\Delta$, i.e., if the decay occurs in accordance with the power law $t^{-\gamma}$, we find that $\gamma\sim T/\Delta$. The continuous curves in Fig. 1 are the $m(t)$ dependences calculated for the case when $T/\Delta=0.1$. The weaker the repulsion between the levels, the longer the decay of the magnetization, since the scatter of the relaxation rates increases as a result of randomization of the distribution of the levels. It follows from Fig. 1 and Eq. (9) that the characteristic time corresponding to $\ln m(t)=-1$ is at least an order of magnitude longer than the relaxation time in a bulk metal T_{sp}.

b) High temperatures, $T\gg\Delta$. The number of electrons in a particle (odd or even) is now unimportant. The relaxation rate of each particle is governed by the contribution of a large number of levels so that self-averaging of the sums in Eq. (8) occurs over different parts of the spectrum. The magnetization of an ensemble of particles then decays exponentially and the relaxation time governed by Eqs. (8) and (10) is found to be equal, irrespective of the nature of the statistics of the levels, to its value T_{sp} for a bulk metal.

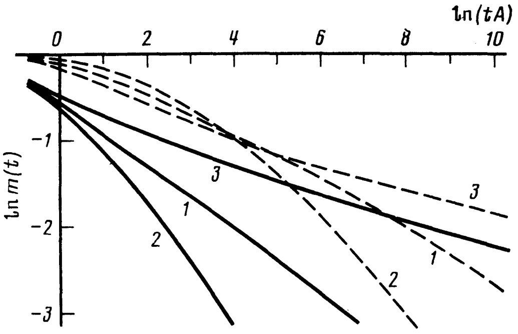

FIG. 1. Decay of the magnetization in the case of continuous (solid curves) and quasidiscrete (dashed curves) phonon spectra of a small particle with different degrees of correlation between the levels: 1) orthogonal ensemble; 2) symplectic ensemble; 3) no correlation.

Therefore, in the case of a continuous phonon spectrum (strong coupling of the metal particles to the matrix) qualitative changes in the relaxation process occur only if $T<\Delta$.

4. QUASIDISCRETE PHONON SPECTRUM

In the case of a weak coupling between the metal and matrix atoms the Hamiltonian of the long-wavelength vibrations of a heterogeneous structure is $H_{ph}=H_1+H_2+H_{12}$, where H_1 describes low-frequency phonons with a discrete set of frequencies ω_q and H_2 describes phonons of a matrix with a continuous spectrum of excitations ω_p. The contribution of the interaction between the metal and the matrix to the vibrational energy can be written in the form

$$H_{12}=\frac{\gamma_{12}}{2a^2}\int ds[\delta R_1(r_s)-\delta R_2(r_s)]^2, \qquad (18)$$

where γ_{12} is the parameter of the interaction between metal and insulator (matrix) atoms; δR_1 and δR_2 are the displacements of the atoms of two kinds near an interface between two media s, which we shall assume to be spherical. If the displacements are expressed in terms of the operators describing the normal vibrations $\varphi_{\mathbf{q}}$ and $\varphi_{\mathbf{p}}$ of the corresponding subsystems, we find that

$$H_{12}=\sum_{p,q}V_{pq}\varphi_{\mathbf{p}}\varphi_{\mathbf{q}},$$

$$V_{pq}=\pi\gamma_{12}(d/a)^2 j_1(pd/2)j_1(qd/2)(\omega_p\omega_q)^{-1}(N_1M_1N_2M_2)^{-1/2}, \qquad (19)$$

where $j_n(x)$ is a spherical Bessel function of the nth order. We retained in Eq. (19) only the terms that cause broadening of the vibrational levels of a metal.

A calculation of the self-energy part of the phonon Green function $D_q(\omega)$ to within the second order with respect to the Hamiltonian of Eq. (19), gives

$$D_q(\omega)=\omega_q^2\{\omega^2-\omega_q^2[1+i\,\mathrm{Im}\,\Sigma_q(\omega)]\}^{-1},$$

$$\mathrm{Im}\,\Sigma_q(\omega)=\frac{3\pi N_2}{2}\left(\frac{\omega}{\omega_{D2}}\right)^3 V_{pq}^2\left(p=\frac{\omega}{u_2}\right). \qquad (20)$$

We omitted the real part $\Sigma_q(\omega)$ which results in weak renormalization of the phonon energies ω_q. It is important to note that as a result of the interaction between the two subsystems the phonon levels of a small particle cease to be sharply defined and acquire a width $\omega_q\,\mathrm{Im}\,\Sigma_q(\omega)$. The spin-phonon relaxation channel becomes stronger as the broadening increases.

Substituting Eqs. (20), (5), and (6) into Eq. (3) and estimating the sum over a discrete set of phonon energies ω_q, beginning from the minimum value $\omega_m = \pi u_i/d$ we find that the relaxation rate τ_{sp}^{-1} is still given by Eq. (8). However, the relaxation parameters A and the power exponents α are now given by

$$A = \frac{2\pi}{15}\frac{1}{T_{sp}}\frac{\Delta}{\omega_m}\left(\frac{\omega_{12}}{2T}\right)^2\left(\frac{\omega_{D1}}{\omega_{D2}}\right)^4 \ln\frac{a}{d}, \qquad \alpha=3 \tag{21}$$

if $\xi_{\lambda'} - \xi_\lambda < \omega_m$ and by

$$A = \frac{8}{5\pi^2}\frac{1}{T_{sp}}\frac{\Delta}{2T}\left(\frac{\omega_{12}}{2T}\right)^2 \ln\frac{2T}{\omega_{12}}, \qquad \alpha=2 \tag{22}$$

if $\omega_{Di} > \xi_{\lambda'} - \xi_\lambda > \omega_m$. Here, ω_{D1} and ω_{D2} are the Debye frequencies of a small particle and of the matrix, respectively, and

$$\omega_{12}=(9\gamma_{12}^2/\pi M_1 M_2 \omega_{D1}\omega_{D2})^{1/2} \sim \omega_D(\gamma_{12}^2/\gamma_1\gamma_2)^{1/2} \ll \omega_D$$

is a characteristic frequency depending on the ratio of the constant of coupling γ_{12} between the atoms of a metal and an insulator to analogous force constants γ_1 and γ_2, respectively, inside the metal and the insulator matrix.

Further calculations associated with determination of the law of decay of the magnetization of an ensemble of small particles are simply repetitions of the calculations described above in the case of a continuous phonon spectrum. At low temperatures such that $T < \Delta$, ω_m, we can compare A and α from Eq. (21) with the corresponding quantities in Eq. (9), and we can see that the relaxation rate $\tau_{sp}^{-1}(\omega)$ of Eq. (13) for an average particle with $\omega \sim \Delta$ is reduced by a factor $(\omega_{12}/\Delta)^2$. The time dependence of the magnetization shown in Fig. 1 by the dashed curves also differs from the case of a continuous phonon spectrum. The discrete nature of the phonon levels then slows down the relaxation process also at high temperatures $T > \Delta$. Substituting Eq. (22) into Eq. (8), we find that $T_i^{-1} \sim T_{sp}^{-1}(\omega_{12}/2T)^2$. The factor in front of T_{sp}^{-1} is essentially the ratio of the rate of decay of phonons $\omega \operatorname{Im}\Sigma(\omega) \sim \omega_{12}^2\omega_m^3/\omega^4$ to the spacing of the phonon levels $\Delta_{\text{ph}}(\omega) \sim \omega_m^3/\omega^2$ at a frequency $\omega \sim 2T$. It should also be noted that the results of this section are valid if $\omega_{12} < \omega_m$ (which is the condition for a quasidiscrete distribution of the levels).

5. SURFACE SPIN RELAXATION

It is natural to assume that the scattering of electrons by spin-orbit surface defects plays a considerable role in small particles. The corresponding contribution of τ_{si}^{-1} to the rate of relaxation can be found by replacing H_{ep} in Eq. (1) with the Hamiltonian

$$H_{si}=\lambda_{so}' \sum_i [\mathbf{n}\mathbf{n}']\mathbf{S}(\mathbf{r}_i), \tag{23}$$

where $\mathbf{S}(\mathbf{r}_i)$ is the operator representing the spin density of electrons at the position of a defect with the coordinate $\mathbf{r}_i$. Then, τ_{si}^{-1} is given by

$$\tau_{si}^{-1} = \frac{(\lambda_{so}')^2}{18\pi}\frac{1}{\chi T}\frac{N_i}{N^2}\sum_{\lambda\neq\lambda_1}\int_{-\infty}^{\infty} d\omega\, \operatorname{ch}^{-2}\left(\frac{\omega}{2T}\right) \times \operatorname{Im} G_\lambda(\omega) \operatorname{Im} G_{\lambda_1}(\omega), \tag{24}$$

where N_i is the number of defects and $G_\lambda(\omega)$ is the retarded Green function of electrons. Following Dyson,[12] it is usual to describe surface relaxation by the probability ε of spin flip of an electron when it collides with the surface. In the case of a massive spherical particle with a quasicontinuous spectrum of electron excitations, it follows from Eq. (24) that

$$\tau_{si}^{-1} = \frac{3\varepsilon v_F}{d}, \qquad \varepsilon = \frac{\pi^2}{3} c_i \left(\frac{\lambda_{so}'}{\varepsilon_F}\right)^2, \tag{25}$$

where v_F is the Fermi velocity and $c_i = N_i/N_s$ is the surface concentration of defects [$N_s = \pi(d/a)^2$ is the number of surface atoms in this particle]. The quantity ε naturally includes a contribution not only of the point defects in accordance with Eq. (23), but also of various surface irregularities, magnetic impurities, etc. If ε is determined by a resonance method, information on the surface of a metal can be obtained.[13]

If the size quantization is allowed for, τ_{si}^{-1} tends to zero because we can no longer satisfy the law of conservation of energy in Eq. (24). Relaxation to static defects is possible only if there is a mechanism that broadens the electron levels. This mechanism can be the electron-phonon interaction represented by the first term in Eq. (2). If we calculate the self-energy part $\Sigma_\lambda(\omega)$ of the function $G_\lambda(\omega)$ in the second order with respect to this interaction, we obtain

$$\begin{gathered} G_\lambda(\omega)=[\omega-\xi_\lambda+i \operatorname{Im}\Sigma_\lambda(\omega)]^{-1}, \\ \operatorname{Im}\Sigma_\lambda(\omega)=\frac{w^2}{2NMu^2}\operatorname{ch}\frac{\omega}{2T}\sum_{\mathbf{q},\lambda'}{}' \left\{|\langle\lambda|e^{i\mathbf{q}\mathbf{r}}|\lambda'\rangle|^2 \operatorname{Im} D_q(\xi_{\lambda'}-\omega) \times\left[\operatorname{ch}\frac{\xi_{\lambda'}}{2T}\operatorname{sh}\left(\frac{\xi_{\lambda'}-\omega}{2T}\right)\right]^{-1}\right\}, \end{gathered} \tag{26}$$

where the prime of a sum denotes that $\lambda' \neq \lambda$. Rewriting Eq. (24) using Eqs. (26), (4), and (25) and following this with simple calculations, we can reduce the formula for τ_{si}^{-1} to a form identical with the right-hand side of Eq. (3) if we assume in this equation that

$$|\langle\lambda\uparrow|U_{\mathbf{q}}|\lambda'\downarrow\rangle|^2 = \frac{3\varepsilon v_F}{d}\frac{1}{2\pi\Delta}\frac{w^2}{NMu^2}|\langle\lambda|e^{i\mathbf{q}\mathbf{r}}|\lambda'\rangle|^2. \tag{27}$$

Since the last two factors in Eq. (27) represent the square of a matrix element of the electron-phonon interaction, the rate of surface spin relaxation in a small particle can be described using Eq. (25) by introducing the effective spin flip probability $\varepsilon_{\text{eff}} \sim \varepsilon/\Delta\tau_{\text{ep}} \ll \varepsilon$ (τ_{ep}^{-1} is the rate of electron energy relaxation via interaction with phonons).

Substituting Eq. (27) into Eq. (3) and repeating the procedures in Sec. 2–4, we can show that the rate of surface relaxation τ_{si}^{-1} is also described by Eq. (8) if the coefficients A and the exponents α are replaced with new values. When phonons in a small particle have a continuous spectrum of excitation, these values are

$$A = \frac{18}{\pi}\frac{\varepsilon v_F}{d}\frac{w^2}{Mu^2\Delta}\left(\frac{2T}{\omega_D}\right)^5, \qquad \alpha=5 \tag{28}$$

if $\xi_{\lambda'} - \xi_\lambda < \omega_m$ and

$$A = \frac{9}{8}\frac{\varepsilon v_F}{d}\frac{w^2}{Mu^2\varepsilon_F}\left(\frac{2T}{\omega_D}\right)^2, \qquad \alpha=2 \tag{29}$$

if $\omega_D > \xi_{\lambda'} - \xi_\lambda > \omega_m$. If the phonon spectrum of a small particle is quasidiscrete, then

$$A=\frac{\pi}{2}\frac{\varepsilon v_F}{d}\frac{w^2}{Mu^2\Delta}\frac{\omega_{12}{}^2}{\omega_{D1}\omega_{D2}}\left(\frac{2T}{\omega_{D2}}\right)^3, \qquad \alpha=3 \tag{30}$$

for $\xi_{\lambda'}-\xi_\lambda<\omega_m$ and

$$A=\frac{9}{2\pi}\frac{\varepsilon v_F}{d}\frac{w^2}{Mu^2\varepsilon_F}\left(\frac{\omega_{12}}{\omega_{D1}}\right)^2\ln\frac{2T}{\omega_{12}}, \qquad \alpha=0 \tag{31}$$

for $\omega_D>\xi_{\lambda'}-\xi_\lambda>\omega_m$. Comparing A and α in Eqs. (28) and (30) with the corresponding expressions for the spin-phonon relaxation given by Eqs. (9) and (21), we find that the temperature dependences and the nature of decay with time are identical for both scattering mechanisms at $T<\Delta$. However, the size dependences are qualitatively different: in the spin-lattice relaxation case we have $A\propto(a/d)^2$, whereas in the surface relaxation case we obtain $A\propto(d/a)^2$.

At temperatures $T\gg\Delta$, substituting Eqs. (29) and (31) into Eq. (8), we find that the rate of relaxation of an ensemble of particles is described by Eq. (25) with the effective probability of spin reversal amounting to

$$\varepsilon_{eff}=\frac{27}{40}\varepsilon\frac{w^2}{Mu^2\varepsilon_F}\left(\frac{2T}{\omega_D}\right)^2\frac{2T}{\Delta} \tag{32}$$

in the case of a continuous phonon spectrum and

$$\varepsilon_{eff}=\frac{3}{2\pi}\varepsilon\frac{w^2}{Mu^2\varepsilon_F}\left(\frac{\omega_{12}}{\omega_{D1}}\right)^2\frac{2T}{\Delta}\ln\left(\frac{2T}{\omega_{12}}\right)\ln\left(\frac{2T}{\omega_m}\right) \tag{33}$$

when the coupling between the particle and medium is weak. It follows from these formulas that if $T>\Delta$, the temperature dependence of the spin relaxation to static defects is somewhat weaker than that due to lattice vibrations. This is due to the absence of the Yafet factor $(qa)^2$, which we mentioned in Sec. 2, in the case of the matrix elements of the electron-phonon scattering without spin flip.

6. LEVEL BROADENING DUE TO THE COULOMB INTERACTION

At low temperatures, particularly in the case of a weak elastic coupling with the surrounding medium, the temperature dependence of the surface relaxation rate may change because of the nonphonon mechanisms of broadening of electron levels. The rate of decay of a quasiparticle of energy $\omega\sim T$, associated with the electron-electron scattering when the transferred energy is of the order of ω, is given by[14]

$$\tau_{ee}{}^{-1}(\omega)\sim\Delta\frac{L_x{}^*}{L_\omega}\frac{L_y{}^*}{L_\omega}\frac{L_z{}^*}{L_\omega}+\frac{\omega^2}{\varepsilon_F}. \tag{34}$$

Here, $L_i^*=\max\{L_i,L_\omega\}$, L_i are the dimensions of the sample, $L_\omega=(D/\omega)^{1/2}$, $D=v_Fl/3$, and l is the mean free path. Equation (34) is derived for an effective dimensionality $d=1$, 2, or 3 defined as the number of measurements for which $L_i>L_\omega$. If we use this formula for a small particle with $d=0$, we find that $\tau_{ee}^{-1}\sim\Delta$. This would mean that the spin relaxation freezing discussed above and associated with the discrete nature of the levels should not occur and, moreover, at energies $\omega\lesssim\Delta$ the quasiparticle description is no longer valid. In reality, we must not substitute $d=0$ in Eq. (34). We shall demonstrate this by considering the example of the contact electron-electron interaction. The corresponding contribution to the imaginary part of the pole of the Green function (26) is

$$\operatorname{Im}\Sigma_\lambda(\omega)\approx\left(\frac{\varepsilon_F}{N}\right)^2\sum_q\sum_{\substack{\lambda_1<0\\ \lambda_2,\lambda_3>0}}|\langle\lambda|e^{i\mathbf{qr}}|\lambda_3\rangle|^2$$

$$\times|\langle\lambda_1|e^{i\mathbf{qr}}|\lambda_2\rangle|^2\delta(\omega+\xi_{\lambda_1}-\xi_{\lambda_2}-\xi_{\lambda_3}). \tag{35}$$

A quasiclassical formula[15]

$$\sum_{\lambda'}|\langle\lambda|e^{i\mathbf{qr}}|\lambda'\rangle|^2\delta(\xi_{\lambda'}-\xi_\lambda-\Omega)$$

$$=g(q,\Omega)=\begin{cases}Dq^2(\Omega^2+D^2q^4)^{-1}, & ql<1\\ (qv_F)^{-1}, & ql>1\end{cases} \tag{36}$$

reduces the decay of Eq. (35) to

$$\gamma(\omega=\xi_\lambda)=\Delta^2\sum_{\lambda'>0}\sum_{q\neq0}\int_{\xi_{\lambda'}}^{\omega}d\Omega g^2(q,\Omega). \tag{37}$$

For $d=1$, 2, and 3 we find that Eq. (37) yields Eq. (34). If $d=0$, it is important to note that the contribution of the interaction with $q=0$ should be excluded, because then the matrix elements in Eq. (35) vanish. In other words, a homogeneous potential (even if it fluctuates in time) cannot give rise to transitions between states because then the energy levels are shifted simultaneously and the separation between them remains unchanged. It is this nonphysical contribution of the homogeneous potential that is responsible for the decay rate $\tau_{ee}^{-1}\sim\Delta$ if we substitute $d=0$ in Eq. (34). A similar situation occurs also in the case of the Coulomb interaction.

For a small particle with $L_x\sim L_y\lesssim L_z$ we find from Eq. (37) that

$$\gamma(\omega)\approx\frac{\omega^2}{\varepsilon_F}+\Delta\begin{cases}(L_z/L_\omega)^4, & L_z<L_\omega\\ L_z/L_\omega, & L_z>L_\omega\end{cases}. \tag{38}$$

In the case of an arbitrary dimension d the decay described by Eq. (37) is

$$\gamma^{(d)}(\omega)\approx\frac{\omega^2}{\varepsilon_F}+\Delta\frac{L_x{}^*L_y{}^*L_z{}^*}{L_\omega{}^3}\int_0^{(L/L_\omega)^4}dx\frac{x^{-d/4}}{1+x}, \tag{39}$$

where L is the maximum size of a sample. Hence, it is clear that in the limit $d\to0$ the integral is determined by the upper limit and there is an additional dependence of the type $(L/L_\omega)^4$. The difference between Eqs. (39) and (34) reduces simply to the corrections which are inversely proportional to the volume of a sample, but which become of fundamental importance on transition to zero-dimensional systems.

The ratio $(L_z/L_\omega)\sim(\alpha\omega/\Delta)^{1/2}$ governing the effective dimensionality of a sample and the nature of decay of quasiparticles depends strongly on the geometry of a sample via the parameter $\alpha=L_za^2/lL_x^2$. If $\alpha<1$ (when the length of a sample does not exceed greatly its thickness) there is a wide zero-dimensional region characterized by $0<\omega<\Delta/\alpha$ and the decay rate is now described by $\gamma(\omega)\ll\omega,\Delta$. In the range $\omega>\Delta/\alpha$ the situation is one-dimensional but we have $\gamma(\omega)\ll\omega$. As the sample becomes longer, we find that $\alpha>1$ when the zero-dimensional range of frequencies is very narrow: $\omega<\Delta/\alpha$, and the decay rate is still less than ω. In the one-dimensional range of energies the quasiparticle description is valid only if $\omega>\alpha\Delta$ whereas for $(\Delta/\alpha)<\omega<\alpha\Delta$ the decay is rapid: $\gamma(\omega)>\omega$. Therefore, the effects of the electron-electron interaction are strong only in the case of anisotropic small particles (pieces of wire, island films) in which diffusion occurs along some direction. In the case of samples characterized by $L_x \sim L_y \sim L_z \sim l$ (and we shall consider only such particles) the decay rate $\gamma(\omega)$ is governed by its classical value ω^2/ε_F and it is less than the phonon contribution to the broadening of levels. It should be mentioned in passing that for $l \sim L_x$ there is again no need for the diffusion renormalization of the interaction with phonons.

We shall now discuss the influence of level broadening because of the interaction with fluctuations of electric fields[16] on surface spin relaxation. The corresponding contribution to the decay of quasiparticles at $T > \Delta$ is calculated in Ref. 17:

$$\tau_N^{-1} \sim T(a/L)^2. \tag{40}$$

At these temperatures we have $T < \omega_D$ and we find that $\tau_N^{-1} \ll \Delta$, which is also small compared with the following contribution if the elastic coupling of the metal to the matrix is not very weak, i.e., if $(\omega_{12}/\omega_D) \gtrsim a/L$. In the opposite case, the formula for the effective probability of spin flip given by Eq. (33) should be supplemented by a quantity of the order of

$$\varepsilon'_{eff} = \varepsilon \frac{T}{\varepsilon_F} \frac{L}{a}. \tag{41}$$

Therefore, the quasiparticle description of small particles is valid at all energies $\omega < \omega_D$ and the broadening of levels is governed primarily by the electron-phonon interaction.

7. CONCLUSIONS

It follows from the above discussion that at temperatures $T < \Delta$ the decay of the magnetization of an ensemble of small particles with time deviates considerably from the exponential law typical of bulk metals. The actual functional dependence m(t) is then governed directly by the nature of the correlation between electron levels. At high temperatures $T > \Delta$ the decay of the total magnetization becomes exponential.

Relaxation of the magnetization and its temperature dependence are governed largely by the nature of the forces of interaction at the metal-insulator interfaces. We can determine whether the phonon spectrum of a small particle is continuous or quasidiscrete from the time dependence $m(t)$ (Fig. 1) and from the temperature dependences of the relaxation parameters A. In the case of a weak coupling between the metal and matrix atoms the relaxation process is strongly suppressed at low and high temperatures.

Separation of the contribution of the spin scattering of electrons by boundary defects can give information on the state of the surface of small metallic particles. Since this relaxation mechanism is possible only in the case of broadening of electron levels because of the interaction with phonons, the effective spin-flip probability ε_{eff} depends on the size of particles and temperature.

The first experimental observation of spin relaxation in small particles of alkali and noble metals with dimensions $d \sim 50$–100 Å, carried out using a pulse method, was reported recently.[18] The main experimental results demonstrating strong suppression of spin relaxation and the nonexponential decay of the total magnetization are in qualitative agreement with the results of our investigation.

We shall conclude by noting that the time dependence of the magnetization $m(t)$ at temperatures $T < \Delta$ may change considerably for systems in which the distances between the metal particles R_0 are so small that the dipole-dipole interaction between the particles described by μ_B^2/R_0^3 becomes of the order of or greater than the reciprocal of the decay time $\tau^{-1}(\omega)$ and find from Eq. (13) that in the case of moderately large particles we have $\omega \sim \Delta$. In this situation the diffusion of nonequilibrium magnetization from weakly relaxing particles to "fast" particles (particles with a suitable spectrum $\omega \sim T < \Delta$ or random particles of large size). The effect of this diffusion is that, depending on the actual situation, we can have different dependences m(t) which will be less extended in time, as shown in Fig. 1.

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