Kinetic phenomena in metals containing two-level systems

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We discuss the interaction of electrons with two-level systems that emerge in some cases when a quantum defect is captured by a heavy immobile impurity. We show that the infrared renormalizations caused by this interaction lead to a nontrivial temperature dependence of the kinetic coefficients of metals containing two-level systems.

As demonstrated by Kondo (see, e.g., Ref. 1), the interaction of electrons in a metal with mobile quantum defects (hydrogen isotopes, helium) leads to strong infrared renormalizations of the Green function of the quantum defects (defectons) and the electron-defecton interaction vertex. As a result the renormalized quantities acquire an additional temperature dependence of the T^g type, with g depending on the properties of the given metal, that is, the dependence is not universal.[1] The value of the rate of electron relaxation caused by electron-defecton scattering, $\tau_{e,d}^{-1}$, differs from that for electrons scattered by randomly "frozen" defects of the same chemical nature, $\tau_{e,dst}^{-1}$, by a factor of $(T/E_0)^g$, with E_0 the width of the electron conduction band.[2]

Such a temperature dependence of the relaxation rate leads to a nontrivial temperature dependence of the metal's kinetic coefficients in the T_K to θ temperature range, where θ is the Debye temperature and T_K the temperature at which the phases with high and low defect concentrations separate.[2–6] For example, the contribution of scattering on defectons to the electrical resistivity has the form

$$\rho=\rho_0\left(\frac{T}{E_0}\right)^g, \tag{1}$$

with ρ_0 the residual resistivity in the case of randomly "frozen" defects of the same chemical nature,[2] and

$$g=2\int\frac{d^3k\,d^3k'\,|V_0(\mathbf{k}-\mathbf{k}')|^2}{(2\pi)^6|\nabla\varepsilon(\mathbf{k})||\nabla\varepsilon(\mathbf{k}')|}, \tag{2}$$

where integration with respect to $\mathbf{k}$ and $\mathbf{k}'$ is over the Fermi surface (FS), $V_0(\mathbf{q})$ is the initial electron-defecton scattering amplitude, and $\varepsilon(\mathbf{k})$ specifies the dispersion for conduction electrons. By order of magnitude $g=2N^2(0)V_0^2$, with $N(0)$ the density of electron states on the FS. For values of $N(0)$ characteristic of metals and $V_0\sim 1$ eV we have $g\sim 1.0$–1.

Defecton clustering, which leads to the defectons becoming "frozen," hinders the observation of nontrivial temperature dependences in the kinetic coefficients of a metal containing quantum defects. In some cases, however, a situation emerges when as a result of a defecton being captured by a heavy fixed impurity a two-level system (TLS) is created. The phenomenon is observed in niobium when hydrogen is captured by heavy impurities such as oxygen, nitrogen, or carbon. The latter occupy the octahedral interstices in the body-centered lattice of niobium, while the hydrogen atoms occupy the tetrahedral interstices. As a result of the interaction with a heavy C, N, or O impurity, a hydrogen atom occupies at $T<150$ K one of the two equivalent equilibrium positions corresponding to the two closest tetrahedral interstices (Fig. 1) (see Ref. 7). A TLS emerges owing to tunneling between these two positions of equilibrium, with the quantum defect partially retaining its mobility below the clustering temperature as well. Hence, it is natural to expect that in this case observation of the nontrivial temperature dependences is possible at $T<T_K$.

The Hamiltonian of a separate TLS has the form

$$\mathscr{H}_{\text{TLS}}=-\frac{\xi}{2}c_1^+c_1+\frac{\xi}{2}c_2^+c_2+\frac{J_0}{2}(c_1^+c_2+c_2^+c_1), \tag{3}$$

where c_j^+ and c_j are second-quantization operators for a defecton in the jth potential well, ξ represents the TLS asymmetry caused by the presence of other crystal defects, and J_0 represents the splitting of the TLS levels caused by tunneling (at $\xi=0$). For hydrogen in niobium J_0 is of the order of 2K (see Ref. 8).

The interaction of the TLS with electrons is described by the Hamiltonian

$$\mathscr{H}_{e\text{-TLS}}=\sum_{j,\mathbf{p},\mathbf{p}'}V_0(\mathbf{p}-\mathbf{p}')a^\dagger(\mathbf{p}')a(\mathbf{p})e^{i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{R}_j}c_j^+c_j, \tag{4}$$

where $a^+(\mathbf{p})$ and $a(\mathbf{p})$ are the electron creation and annihilation operators, summation with respect to $\mathbf{p}$ and $\mathbf{p}'$ is over the first Brillouin zone, and $\mathbf{R}_j$ represents the coordinates of the TLS minima.

Diagonalizing $\mathscr{H}_{\text{TLS}}$ yields

$$\mathscr{H}_{\text{TLS}}=\sum_{j=1,2}(-1)^j\frac{E}{2}\tilde{c}_j^+\tilde{c}_j, \tag{5}$$

where

$$\begin{gathered}E=\sqrt{\xi^2+J_0^2},\\ \tilde{c}_1=ac_1-bc_2,\quad \tilde{c}_2=ac_2+bc_1,\\ a=\sqrt{0.5\left(1+\frac{\xi}{E}\right)},\quad a=\sqrt{0.5\left(1-\frac{\xi}{E}\right)}.\end{gathered} \tag{6}$$

In terms of this basis the Hamiltonian $\mathscr{H}_{e\text{-TLS}}$ assumes the form

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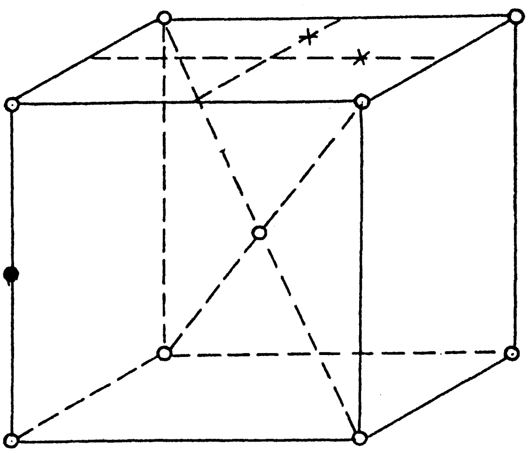

FIG. 1. A two-level system in a niobium single crystal: ○ correspond to niobium atoms, ● stands for a heavy impurity atom, and the × designate the equilibrium positions of hydrogen atoms.

$$\mathscr{H}_{e\text{-TLS}}=\sum_{j,\mathbf{p},\mathbf{p}'} V_0(\mathbf{p}-\mathbf{p}')a^+(\mathbf{p}')a(\mathbf{p})\{e^{i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{R}_1}[a^2\tilde{c}_1^+\tilde{c}_1 + b^2\tilde{c}_2^+\tilde{c}_2+ab(\tilde{c}_2^+\tilde{c}_1+\tilde{c}_1^+\tilde{c}_2)] + e^{i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{R}_2}[a^2\tilde{c}_2^+\tilde{c}_2+b^2\tilde{c}_1^+\tilde{c}_1 - ab(\tilde{c}_2^+\tilde{c}_1+\tilde{c}_1^+\tilde{c}_2)]\}. \quad (7)$$

Calculating the infrared renormalizations of the initial defecton Green function and V_0 is a fairly simple task for $k_F a \ll 1$, where $\mathbf{a}=\mathbf{R}_2-\mathbf{R}_1$, when we can assume that $e^{i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{R}}=1$ in Eq. (7). The procedure is similar to that used in studies of the anomalies in the x ray emission and absorption spectra.[9]

In the parquet approximation ($g^{3/2}\ln(E_0/T)\ll 1$) and in the $T \gg E$ temperature range, the quantum-defecton Green function $\psi_{j,j}(\varepsilon_k)$ is given by the following expression:

$$\Psi_{j,j}(\varepsilon_k)=\frac{1}{i\varepsilon_k-(-1)^j E/2+\zeta}\left(\frac{T}{E_0}\right)^g, \quad (8)$$

where ε_k is the Matsubara frequency, ζ is the chemical potential of defectons, and

$$V(\mathbf{k})=V_0(\mathbf{k})\left(\frac{T}{E_0}\right)^g. \quad (9)$$

In this approximation the renormalizations of J_0 and E can be ignored.

The most divergent parquet diagrams for the self-energy part of $\Psi_{j,j}(\varepsilon_k)$ and for $V(\mathbf{k})$ are depicted in Figs. 2 and 3, respectively. All vertices except the initial are equal to V_0 and are diagonal in j.

Let us estimate the asymmetry of TLS on the basis of the assumption that the asymmetry is caused by the presence of randomly distributed frozen defects of concentration c and that the contribution of mobile defects to the asymmetry is small compared to that of the heavy impurities. In the opposite case collective effects in the system of mobile defects become important.

The resulting long-range interaction between impurities is given by the sum

$$W(\mathbf{R})=E_{\text{elas}}(\mathbf{R})+\tilde{W}_{\text{el}}(\mathbf{R}), \quad (10)$$

where $W_{\text{elas}}(\mathbf{R})$ is the elastic interaction between defects,

$$W_{\text{elas}}(\mathbf{R})=\frac{W(\mathbf{b})\Omega}{R^3}, \quad (11)$$

$\tilde{W}_{\text{el}}(\mathbf{R})$ is the interaction via Friedel oscillations of the electron density, $\mathbf{R}$ the distance between defects, Ω the elementary cell volume, and $\mathbf{b}=\mathbf{R}/R$. Depending on the orientation of vector $\mathbf{b}$ in relation to the crystal-lattice axes, $W(\mathbf{b})$ is either positive or negative, and

$$\tilde{W}_{\text{el}}(\mathbf{R})=\frac{\Omega N(0)\,|V_0(2k_{\text{F}})|^2\cos 2k_F R}{2\pi\varepsilon^2(2k_{\text{F}},0)R^3}, \quad (12)$$

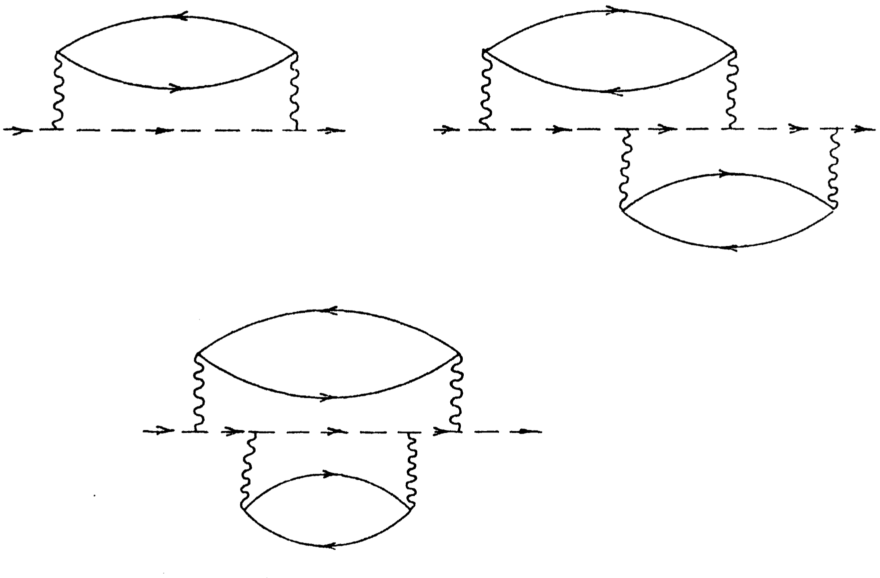

FIG. 2. Diagrams for the self-energy part of the defecton Green function. The solid and dashed lines depict the zeroth Green functions of electrons and defectons, respectively, and the wavy line the $V_0(\mathbf{q})$ interaction.

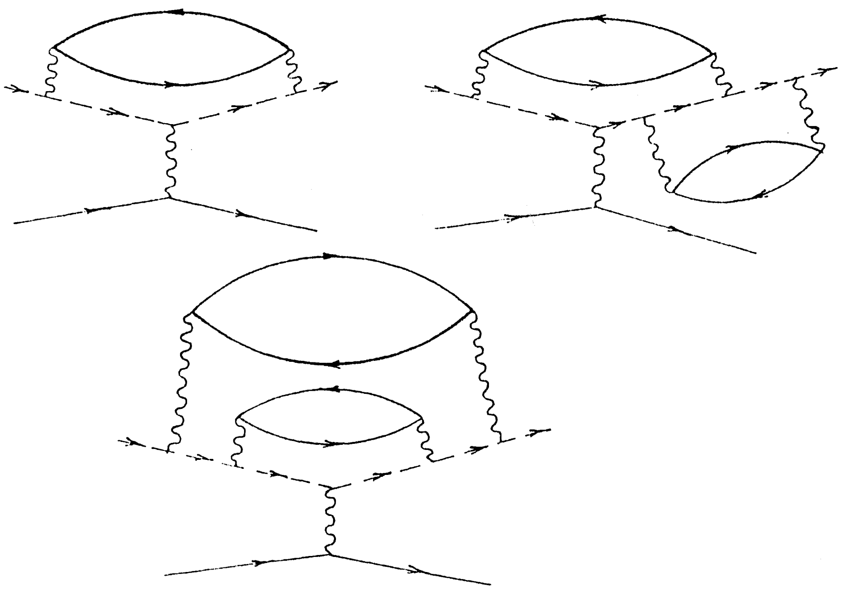

FIG. 3. Diagrams for the vertex of the electron-defecton interaction $V(\mathbf{q})$.

where k_F is the Fermi momentum, and $\varepsilon(\mathbf{k},0)$ the static dielectric constant. For the interaction between defects of different types, $|V_0(2k_F)|^2$ must be replaced by

$$\tfrac{1}{2}[V_{0,1}(2k_F)V^*_{0,2}(2k_F)+\text{c.c.}],$$

where the subscripts 1 and 2 refer to the type of impurities.

The quantity ξ is given by the formula

$$\xi=\sum_{m\neq i}[W(\mathbf{R}_m-\mathbf{R}_2)-W(\mathbf{R}_m-\mathbf{R}_1)], \qquad (13)$$

where summation is over the coordinates $\mathbf{R}_m$ of all the TLS except the chosen one.

The reader can easily see that because of the rapid variation of $\cos 2k_FR$ the main contribution to ξ is provided by the interaction via Friedel oscillation of the electron density (the elastic-interaction contribution contains the smallness parameter d/R):

$$\xi=\sum_m \frac{N(0)\Omega[V_1^{(0)}(2k_F)V_2^{(0)}(2k_F)+\text{c.c.}]}{2\pi\varepsilon^2(2k_F,0)|\mathbf{R}-\mathbf{R}_m|^3} \times\sin\left[\frac{k_F(\mathbf{a},\mathbf{R}-\mathbf{R}_m)}{|\mathbf{R}-\mathbf{R}_m|}\right]\sin(2k_F|\mathbf{R}-\mathbf{R}_m|), \qquad (14)$$

where $\mathbf{R}=\mathbf{R}_1+\frac{1}{2}\mathbf{a}$, and summation is over fixed (stationary) defects with coordinates $\mathbf{R}_m$.

Since $\sin 2k_F|\mathbf{R}-\mathbf{R}_m|$ rapidly oscillates over atomic distances, we consider a simplified model in which we assume that the product of sines in Eq. (14) assumes a value in the interval $(-k_Fa, k_Fa)$ with a probability independent of $|\mathbf{R}-\mathbf{R}_m|$.

In this case the problem of the distribution of ξ is similar to that of the dipole magnetic-resonance linewidth.[10] in the $c\ll 1$ range the distribution of ξ is Lorentzian with a characteristic width

$$\delta=cW_{\text{el}}(d)k_Fa. \qquad (15)$$

TLS asymmetry can also be formed by elastic interaction. Deforming the lattice lifts the degeneracy of the TLS minima in energy. This leads to TLS asymmetry equal to

$$\xi=\gamma u, \qquad (16)$$

where γ is of the order of atomic energy if crystallographically the interstices are not equivalent, and of the order of the defecton-heavy impurity binding energy if they are crystallographically equivalent. Since the deformation generated by a point defect falls off like $u_0\Omega/R^3$ as the distance R increases, the asymmetry caused by this deformation also falls off like R^{-3}. The final expression is

$$\delta=c[W_{\text{elas}}(d)+W_{\text{el}}(d)k_Fa]. \qquad (17)$$

The interaction of TLS with other defects changes the quasiclassical action S, which determines the tunneling probability, by an amount S':

$$S=S_0+S'. \qquad (18)$$

In order of magnitude, $S_0=\sqrt{M/m}$, where M is the mass of the tunneling particle, and m the electron mass ($\hbar=1$) (see Ref. 11). There are two contributions to S'. One is due to the interaction $W_{\text{el}}(\mathbf{R})$ and is, by order of magnitude, equal to $S_0k_FaW_{\text{el}}(\mathbf{R})/U_0$, where U_0 is the height of the potential barrier between the TLS minima, while the other is due to the deformation generated by defects near the TLS and is, in order of magnitude, equal to $(\partial S_0/\partial u)u_0\Omega/R^3$. For characteristic values of R of the order of $dc^{1/3}$,

$$S'=S\frac{\delta}{U_0}\sim\frac{\delta}{\omega_0}\ll 1, \qquad (19)$$

where ω_0 is the local frequency of defecton oscillations in an interstice. Since $S'\ll 1$, we can neglect the spread of values of J_0 in a crystal with a low defect density ($c\leqslant 10^{-2}$) (see Ref. 12).

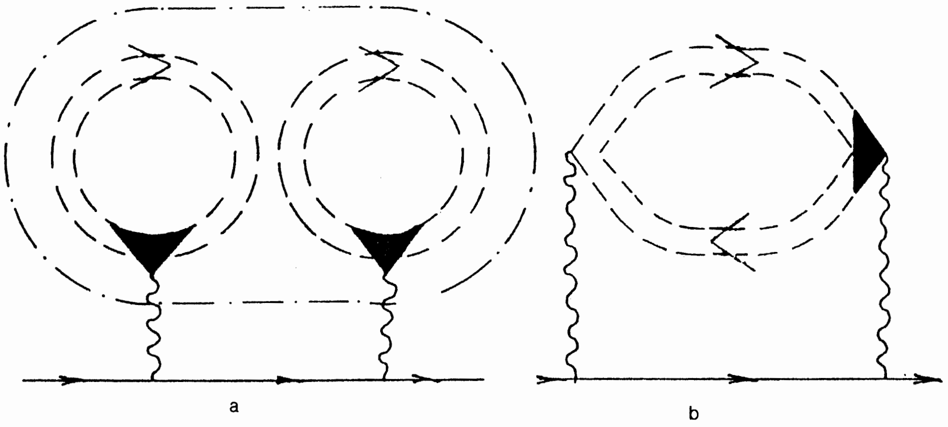

FIG. 4. Diagrams for the self-energy part of the electron Green function. A double dashed line corresponds to $\Psi_{j,j}(\varepsilon_k)$, a wavy line with a full triangle at one end corresponds to $V(\mathbf{q})$, and a dot-dash oval signifies that all defecton bubbles encompassed by it belong to the same TLS.

Let us now consider the contribution of TLS to electron damping. This is determined by the diagrams in Fig. 4. If two Green functions in the defecton bubble depicted in Fig. 4(b) correspond to states with different energies, the respective inelastic contribution to resistivity contains, compared to the elastic contribution (when two Green functions correspond to the same state), an additional small term $(k_Fa)^2$, which can be ignored.

To within terms of the order of $(k_Fa)^2$ we get

$$\tau_{e,d}^{-1}(\mathbf{k})=\sum_m\int\frac{d^3k'\,|V_0(\mathbf{k}-\mathbf{k}')|^2}{\Omega(2\pi)^2|\nabla\varepsilon(\mathbf{k}')|}\times\left[1+2N_m(1-N_m)\left(\frac{T}{E_0}\right)^g\right], \tag{20}$$

where N_m is the occupation number of the lower level in the mth TLS.

Similarly, for the resistivity we have

$$\rho=\rho_0\left[1+\frac{2\Omega}{x_{\text{TLS}}\tilde{v}}\sum_m N_m(1-N_m)\left(\frac{T}{E_0}\right)^g\right], \tag{21}$$

where $\tilde{v}$ is the volume of the system, and

$$N_m=\frac{\exp(E_m/T)}{1+\exp(E_m/T)} \tag{22}$$

Here we have not allowed for the contribution to electron scattering introduced by heavy immobile impurities. In addition to the additive contribution of these impurities to $\tau_{e,d}^{-1}$ and ρ, there is an interference contribution to the scattering, depicted in Fig. 5. This contribution is temperature independent and influences the constant component in ρ.

Let us find the coefficient of $(T/E_0)^g$, using the fact that the distribution of ξ is Lorentzian. If $\delta\gg J_0$, then

$$\frac{2\Omega}{x_{\text{TLS}}\tilde{v}}\sum_m N_m(1-N_m)=\langle N(1-N)\rangle$$
$$=\frac{\delta}{4\pi}\int\frac{d\xi}{\xi^2+\delta^2}\cosh^{-2}\left(\frac{\sqrt{\xi^2+J_0^2}}{2T}\right)$$
$$=\begin{cases}0.25 & \text{if } T\gg\delta,\\ T/\pi\delta & \text{if } \delta\gg T\gg J_0,\\ \sqrt{2J_0T/\pi}\,\delta^{-1}e^{-J_0/T} & \text{if } J_0\gg T,\end{cases} \tag{23}$$

where the angle brackets stand for averaging over the TLS. When $J_0\gg\delta$, we have

$$\langle N(1-N)\rangle=\begin{cases}0.25\cosh^{-2}(J_0/2T) & \text{if } T\gg\delta^2/2J_0,\\ \sqrt{2J_0T/\pi}\,\delta^{-1}e^{-J_0/T} & \text{if } \delta^2/2J_0\gg T.\end{cases} \tag{24}$$

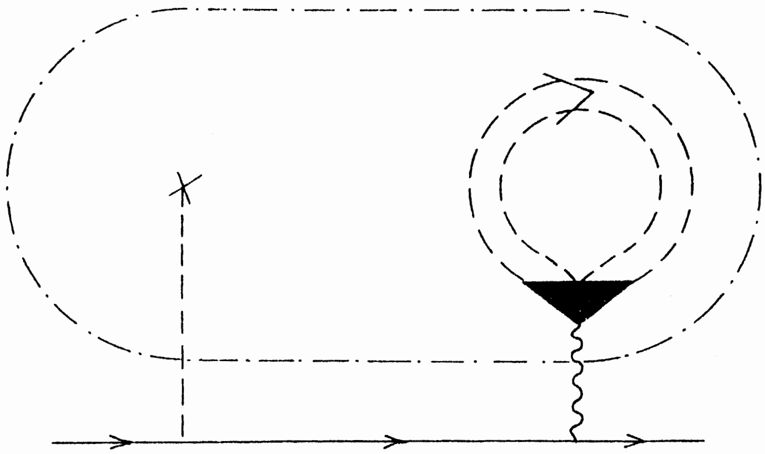

FIG. 5. The interference contribution to the self-energy part of the electron Green function. The × corresponds to scattering on an immobile defect, and the dot-dash oval signifies that the quantum and fixed defects belong to the same TLS.

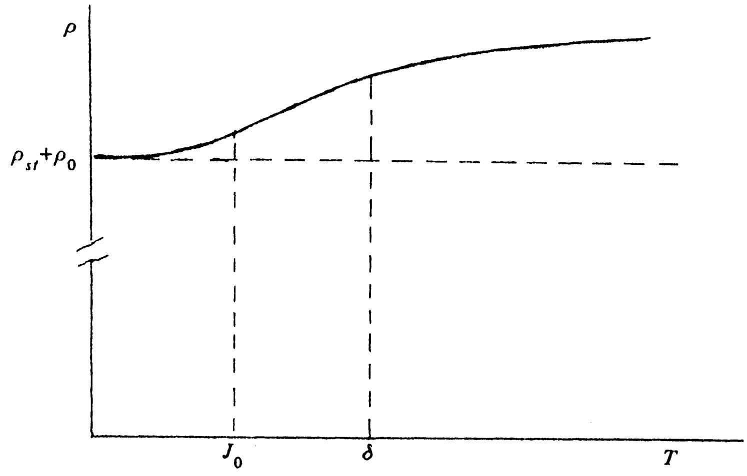

FIG. 6. The temperature dependence of the TLS contribution to the resistivity of a metal.

Thus, in the temperature range from T_K to $\max(\delta, J_0)$ the expression for $\tau_{e,d}$ has the form $\tau_{e,d}^{-1}=A+B(T/E_0)^g$, where A and B are constants of the same order of magnitude. Since at temperatures much lower than the Debye temperature the TLS contribution to the electron relaxation rate is predominant, such a $\tau_{e,d}$ dependence leads to anomalous temperature dependences for the kinetic coefficients of metals containing TLS. For instance, for the TLS contribution to the resistivity we have

$$\rho=\rho_{st}+\rho_0\left[1+0.5\left(\frac{T}{E_0}\right)^g\right], \qquad (25)$$

where ρ_{st} is the contribution to resistivity from immobile defects and from interference. The temperature dependence of ρ is depicted in Fig. 6. For $g \sim 0.3$, $E \sim 3\times10^4$ K, and $T \sim 30$ K, the temperature-dependent term in ρ amounts to several percent.

Experimental studies of the temperature dependence of resistivity of $Nb(OH)_x$, $Nb(NH)_x$, and $Nb(CH)_x$ compounds are undoubtedly of interest.

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