Paramagnetic relaxation due to plasma oscillations of the current carriers

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Paramagnetic relaxation of impurity centers in solids, due to interaction between the centers and Langmuir oscillations of the carrier plasma, is considered. The dependences of the relaxation transition probabilities on transition frequency, carrier density, and temperature are obtained. The theory is consistent with the paramagnetic relaxation pattern observed experimentally in semiconductors.

INTRODUCTION

Spin-lattice relaxation of paramagnetic ions in semiconductors, due to the influence of electric fields of crystal defects (which can themselves be magnetic centers) was considered earlier in[1,2]. It was assumed there that the electric fields corresponding to particular defect types (pointlike ions, dipoles, charged filaments) are modulated by the crystal-lattice vibrations and act on the orbital motion of the paramagnetic-center electron. Owing to the spin-orbit coupling, such an action can lead to relaxation transitions in the spectrum of the paramagnetic impurity. Fluctuations in the carrier charge density are produced in crystals by alternating fields which, according to[1], can stimulate paramagnetic relaxation. We are dealing thus with interaction between a solid-state plasma and paramagnetic centers. Transitions between magnetic impurity levels are accompanied by absorption or emission of plasmons.

We note that a possible mechanism of carrier recombination in semiconductors, based on similar considerations, has already been proposed (see, e.g.,[3]). Of course, from the entire manifold of plasma oscillations, the only ones of importance for relaxation processes of the type considered in[1,2] are those accompanied by fluctuations of the electric fields. Agreement between the transition frequency and the oscillation frequency (which is essential for single-quantum processes) is quite easily reached, since the carrier density can be varied in a wide range. This, in particular, is the situation in semiconductors.

In this paper we consider, by way of example, the direct process of paramagnetic relaxation of deep donor centers in semiconductors, a relaxation that occurs under the influence of the fluctuating electric field of the carrier plasma. We note that the semiconductor plasma can be regarded as isotropic and unmagnetized at the external magnetic field intensities used in radio spectroscopy at centimeter wavelengths. We confine ourselves also to the case of a single-component (electron) plasma.

1. PROBABILITIES OF RELAXATION TRANSITIONS

The interaction of a paramagnetic center with an alternating electric field can be described by the spin Hamiltonian

$$\hat{\mathscr{H}}_1(\mathbf{R},t)=\sum_{ijk}\alpha_{ijk}E_i(\mathbf{R},t)\{\hat{S}_j\hat{S}_k\}+\sum_{ijk}\beta_{ijk}H_iE_j(\mathbf{R},t)\hat{S}_k, \qquad (1)$$

where α_{ijk} and β_{ijk} are the component of the tensor of the electric-field effect; $E_i(\mathbf{R}, t)$ are the components of the electric field intensity at the observation point $\mathbf{R}$ and at the instant of time t; H_i are the components of the intensity of the external magnetic field: $(i, j, k) = (x, y, z)$, $\{\hat{S}_j\hat{S}_k\} = \hat{S}_j\hat{S}_k + \hat{S}_k\hat{S}_j$, and $\mathbf{S}$ is the ion spin operator. It is understood that the position of the paramagnetic ion in the lattice is not an inversion center.

Assume that the crystal contains free carriers of like sign[1)] (electrons or holes) with a concentration n. The fluctuating charge density due to displacements of these carriers is[4]

$$\rho(\mathbf{r},t)=-ne\Delta(\mathbf{r})=-ne\sum_{\mathbf{k}}ik\left(\frac{\hbar}{2Nm\omega_{\mathbf{k}}}\right)^{1/2}(a_{\mathbf{k}}e^{i\mathbf{k}\mathbf{r}}-a_{\mathbf{k}}^{+}e^{-i\mathbf{k}\mathbf{r}}). \qquad (2)$$

Here $\Delta(\mathbf{r})$ is the "volume expansion operator" for small oscillations, Nm is the mass of the oscillating carriers, and a_k (a_k^+) is the annihilation (creation) operator for a plasmon of frequency ω_k and momentum $\hbar k$.

The potential produced by the charge density (2) at the observation point is obviously equal to

$$V(\mathbf{R},t)=\frac{4\pi ne}{\varepsilon}\left(\frac{\hbar}{2Nm}\right)^{1/2}i\sum_{\mathbf{k}}k^{-1}\omega_{\mathbf{k}}^{-1/2}(a_{\mathbf{k}}^{+}e^{-i\mathbf{k}\mathbf{R}}-a_{\mathbf{k}}e^{i\mathbf{k}\mathbf{R}}), \qquad (3)$$

where ϵ is the dielectric constant of the crystal.

Taking (3) into account, the interaction operator $\hat{\mathscr{H}}_1(\mathbf{R}, t)$ takes the form

$$\hat{\mathscr{H}}_1(\mathbf{R},t)=\frac{4\pi ne}{\varepsilon}\left(\frac{\hbar}{2Nm}\right)^{1/2}\sum_{\mathbf{k}}k^{-1}\omega_{\mathbf{k}}^{-1/2}(a_{\mathbf{k}}^{+}e^{-i\mathbf{k}\mathbf{R}}-a_{\mathbf{k}}e^{i\mathbf{k}\mathbf{R}})\times\Big[\sum_i k_i\hat{Q}_i+\sum_j k_j\hat{P}_j\Big]. \qquad (4)$$

Here

$$\hat{Q}_i=\sum_{jk}\alpha_{ijk}\{\hat{S}_j\hat{S}_k\},\quad \hat{P}_j=\sum_{ik}\beta_{ijk}H_i\hat{S}_k. \qquad (5)$$

The probability of a direct relaxation transition between the magnitude levels of the impurity ion ($a \to b$) under the influence of (4) is equal to (the transition is accompanied by the appearance of one plasmon)

$$W(a\to b)=\frac{2(2\pi)^3n^2e^2k_0T}{\hbar^2\varepsilon^2Nm}\sum_{\mathbf{k}}\frac{\omega_k^{-2}}{k^2}\Big|\sum_i k_i(\hat{Q}_i)_{ba}+\sum_j k_j(\hat{P}_j)_{ba}\Big|^2\delta(\omega_{\mathbf{k}}-\omega_{ab}). \qquad (6)$$

We have carried out here a statistical averaging in the plasmon system, and used the "high-temperature approximation" $\bar{n}_k + 1 \sim k_0T/\hbar\omega_k$; ω_{ab} is the transition frequency.

By way of example, we consider crystals with symmetry T_d. Then $\alpha_{ijk} = \alpha_0$, $\beta_{ijk} = \beta_0$, and expression (6) takes the form

$$W(a\to b)=\frac{2(2\pi)^3 n^2e^2k_0T}{\hbar^2\varepsilon^2 Nm}[\alpha_0^2L_{ba}^{(1)}+\beta_0^2L_{ba}^{(2)}+2\alpha_0\beta_0\operatorname{Re}L_{ba}^{(3)}]$$
$$\cdot\sum_{\mathbf{k}}(k\omega_{\mathbf{k}})^{-2}\sum_{l,l'}k_lk_{l'}\delta(\omega_{\mathbf{k}}-\omega_{ab})\qquad (l,l')=(x,y,z). \tag{7}$$

We have introduced in (7) the notation

$$L_{ba}^{(1)}=\sum_{jk}|\{\hat S_j\hat S_k\}_{ba}|^2,\qquad L_{ba}^{(2)}=\sum_{ik}|H_i(\hat S_k)_{ba}|^2,$$
$$L_{ba}^{(3)}=\sum_{jk}\{\hat S_j\hat S_k\}_{ba}\sum_{i'k'}H_{i'}(\hat S_{k'})_{ba}^{*}. \tag{8}$$

The summation over $\mathbf{k}$ in (7), carried out by a transition to integration

$$\sum_{\mathbf{k}}\to(2\pi)^{-3}V\int d\mathbf{k},$$

yields for Langmuir plasma-carrier oscillations ($\omega_k^2 = \Omega^2 + {}^3\!/_2k^2s^2$, $\Omega^2 = 4\pi ne^2/\epsilon m$, $s^2 = 2k_0T/m$)

$$W(a\to b)=2(^2/_3)^{5/2}[\alpha_0^2L_{ba}^{(1)}+\beta_0^2L_{ba}^{(2)}+2\alpha_0\beta_0\operatorname{Re}L_{ba}^{(3)}]$$
$$\times\frac{k_0T\Omega^2}{\hbar^2\varepsilon s^3}\left(1-\frac{\Omega^2}{\omega_{ab}^2}\right)^{1/2},\quad \Omega<\omega_{ab}<2\Omega. \tag{9}$$

This expression can be obtained in another manner by using the theory of quantum transitions induced by perturbations that are random functions of the time (see, e.g.,[5]). In this case the transition probability is expressed in terms of the Fourier transforms of the correlation functions of the electric-field intensity components:

$$W(a\to b)=\hbar^{-2}[\alpha_0^2L_{ba}^{(1)}+\beta_0^2L_{ba}^{(2)}+2\alpha_0\beta_0\operatorname{Re}L_{ba}^{(3)}]\sum_{ll'}\langle E_lE_{l'}\rangle_{\omega_{ab}}. \tag{10}$$

Using (3), we express the correlation function in the form

$$\langle E_l(\mathbf{R},t)E_{l'}(\mathbf{R}',t')\rangle=\frac{8\pi^2\hbar n^2e^2}{Nm\varepsilon^2}\sum_{\mathbf{k},\mathbf{k}'}(\omega_{\mathbf{k}}\omega_{\mathbf{k}'})^{-1/2}\frac{k_lk_{l'}}{k^2}\langle(b_{\mathbf{k}}^+\exp(-i\mathbf{k}\mathbf{R}+i\omega_{\mathbf{k}}t)$$
$$+\text{c.c.})(b_{\mathbf{k}'}^+\exp(-i\mathbf{k}'\mathbf{R}'+i\omega_{\mathbf{k}'}t')+\text{c.c.})\rangle. \tag{11}$$

The angle brackets $\langle\ \rangle$ denote averaging over the quantum-mechanical state of the plasmon system and over the statistical distribution of these states; b_k^+ and b_k are the Bose amplitudes.

In the high-temperature approximation we have

$$\langle E_lE_{l'}\rangle_{\rho,\tau}=\frac{8\pi^2n^2e^2k_0T}{Nm\varepsilon^2}\sum_{\mathbf{k}}\frac{k_lk_{l'}}{(k\omega_k)^2}[\exp(-ik\rho+i\omega_k\tau)+\text{c.c.}],$$
$$\rho=\mathbf{R}-\mathbf{R}',\quad \tau=t-t'. \tag{12}$$

The Fourier transform of the autocorrelation function ($\rho = 0$) is

$$\langle E_lE_{l'}\rangle_{0,\omega}=\frac{8\pi^2n^2e^2k_0T}{Nm\varepsilon^2}\sum_{\mathbf{k}}\frac{k_lk_{l'}}{(\omega_{\mathbf{k}}k)^2}[2\pi\delta(\omega_{\mathbf{k}}+\omega)+2\pi\delta(\omega_{\mathbf{k}}-\omega)]. \tag{13}$$

For the Langmuir oscillations we obtain (taking only emission processes into account)

$$\langle E_lE_{l'}\rangle_{0,\omega}=\left(\frac{2}{3}\right)^{5/2}\frac{k_0T\Omega^2}{\varepsilon s^3}\delta_{ll'}\left(1-\frac{\Omega^2}{\omega^2}\right)^{1/2}. \tag{14}$$

We see that only the autocorrelation-function Fourier transforms that connect identical components of the electric field intensity vector differ from zero. Substitution of (14) in (10) leads to a result that coincides, naturally, with (9).

As a check, let us determine $\langle E_lE_{l'}\rangle_\omega$ by using the fluctuation-dissipation theorem. For an equilibrium isotropic plasma, the spectral distribution of the electric-field fluctuations at high temperatures is (see, e.g.,[6])

$$\langle E_lE_{l'}\rangle_{\mathbf{k}\omega}=\frac{8\pi k_0T}{\omega\varepsilon}\left\{\frac{k_lk_{l'}}{k^2}\frac{\operatorname{Im}\varepsilon_l}{|\varepsilon_l|^2}+\left(\delta_{ll'}-\frac{k_lk_{l'}}{k^2}\right)\frac{\operatorname{Im}\varepsilon_t}{|\varepsilon_t-(ck/\omega)^2|^2}\right\}, \tag{15}$$

where ϵ_l and ϵ_t are respectively the longitudinal and transverse dielectric constants of the carrier plasma. It can be shown that the principal role in (15) is played by the first term (allowance for the second term yields a correction of the order of $(s/c)^2$, where c is the speed of light)[2]. For long-wave oscillations ($ak \ll 1$) (a is the Debye radius) we have

$$\langle E_lE_{l'}\rangle_{\mathbf{k}\omega}=\frac{8\pi k_0T\Omega^2}{\omega\varepsilon}\frac{k_lk_{l'}}{k^2}\delta(\omega^2-\omega_{\mathbf{k}}^2). \tag{16}$$

We again obtain accordingly the expression (14) for the frequency distribution of the fluctuations (by integrating (16) with respect to $(2\pi)^{-3}d\mathbf{k}$).

Attention is called to the fact that in formula (9) the probability of the direct relaxation process is inversely proportional to the cube of the oscillation propagation velocity, in contrast to the v^{-5} dependence (v is the speed of sound) obtained for the corresponding spin-phonon process. This is a reflection of the difference between the character of the onset of the plasma and photon dissipative systems.

2. DEPENDENCE OF W (a → b) ON THE EXTERNAL MAGNETIC FIELD, ON THE CARRIER DENSITY, AND ON THE TEMPERATURE

As follows from (8) in the example considered above, with T_d symmetry, relaxation transitions are possible between the Zeeman levels of the paramagnetic ion, with selection rules $\Delta M = M_a - M_b = 1$ or 2 (M_a and M_b are the corresponding eigenvalues of the operator $\hat S_z$), Therefore $\omega_{ab} = (1; 2)g\beta H_z/\hbar$, where β is the Bohr magneton. Equation (9) can then be represented in the form (we assume for simplicity that H is parallel to the axis z of the crystallographic coordinate system)

$$W(a\to b)\sim\begin{cases}C_1(1-H_0^2/4H^2)^{1/2}, & |\Delta M|=2\\ (C_1+C_2H^2+C_3H)(1-H_0^2/H^2)^{1/2}, & |\Delta M|=1\end{cases} \tag{17}$$

We have put here $H_0 = \hbar\Omega/g\beta$; C_1, C_2, and C_3 are dimensional constant factors. The rate of variation of H is determined by the limits of the applicability of formula (9), namely, $\Omega < \omega_{ab} < 2\Omega$. We see that when the transition frequency coincides with the plasma frequency Ω ($H = H_0$ and $H = H_0/2$ for $\Delta M = 1$ and 2, respectively), the corresponding probability of the relaxation-transition vanishes. This is a consequence of the vanishing of the density of the plasma oscillations with frequency Ω. Let us note the qualitative difference between (17) and the corresponding relations for spin-phonon relaxation processes. Substituting the explicit expression for the plasma frequency Ω in (9), we obtain

$$W(a\to b)\sim C_0n(1-n/n_0)^{1/2}, \tag{18}$$

where $n_0 = \omega_{ab}^2 m\epsilon/4\pi e^2$, and C_0 is a dimensional factor. We see that $W(a\to b)$ is maximal at $n = 2n_0/3$, and vanishes at $n = n_0$ (it was noted above that the oscillation-density corresponding to the plasma frequency is equal to zero).

The concentration dependence of $W(a\to b)$ is closely related to the temperature dependence. Indeed, expression (9) contains, besides the proportionality to T, which is typical of single-quantum relaxation processes, also an implicit temperature dependence via the functions $s = s(T)$ and $n = n(T)$. The last of these functions can be different in semiconductors. Thus, for example, assuming that the carriers have appeared in the conduction band as a result of thermal ionization of the donors, we obtain

$$W(a\to b)\sim T^{3/4}\exp(-E_D/2k_0T), \qquad (19)$$

where E_D is the donor ionization energy reckoned from the bottom of the conduction band. We note that the transition probability can depend, via n, on the degree of compensation of the sample.

3. COMPARISON WITH EXPERIMENT

We consider paramagnetic relaxation of the iron-group ions in silicon. The choice of just these objects is governed by the fact that their EPR spectra have been well studied, their relaxation times were measured, and the electric-field effects in EPR were also investigated for them (a detailed bibliography is given in[7,8]).

Ions of the iron group produce deep energy levels in the forbidden band of silicon. Different charge states of the impurity centers are obtained by changing the concentration of the shallow donors (or acceptors) in the initial silicon. The latter can thus be effective suppliers of carriers to the conduction band even at low temperatures. The spectra of the ions $Cr^+(3d^5)$ and $Fe^0(3d^8)$ were well observed at $T = 20.4°K$ and sometimes at $T = 78°K$, thus evidencing relatively large relaxation times. It is precisely for these ions that $\beta_0 \sim 0$ and the values of α_0 are small[9]. The spectra of the ions $Cr^0(3d^6)$, $Mn^+(3d^6)$, $Mn^0(3d^7)$, $Fe^+(3d^7)$ at $T \lesssim 10°K$ consist of broad lines corresponding to relaxation times shorter than one second. A comparison of the observed relaxation times with those calculated with the aid of (9) shows good agreement. Thus, for reasonable values of the plasma parameters we have $W(Cr^0) \sim 2.5\ sec^{-1}$, $W(Mn^+) \sim 30.0\ sec^{-1}$, and $W(Fe^+) \sim 0.7\ sec^{-1}$. We note that in order of magnitude the relaxation times are accounted for also by the mechanisms considered in[1,2], which have field and temperature dependences different from (17) and (19). The absence of corresponding experimental data makes it difficult to separate any one concrete mechanism. It is known, however, that when the temperature is raised above 10°K it is impossible to observe EPR spectra of the ions Cr^0, Mn^+, Mn^0, and Fe^+. This indicates the existence of a paramagnetic-relaxation mechanism whose efficiency depends strongly on the temperature. It is this kind of temperature dependence that we have obtained for the relaxation time.

The characteristic temperature dependence of the relaxation time $\tau_S \sim \exp(\mathcal{E}/k_0T)$ was observed for phosphorus in silicon[10], but unfortunately the values of the electric-field constants for the shallow donors in silicon are unknown, and a quantitative comparison of the theoretical temperature dependence with the experimental one is impossible.

The foregoing gives ground for concluding that the Langmuir oscillations of the carrier plasma in semiconductors can play an important role in paramagnetic relaxation processes and can explain, in particular, the relaxation of the deep donor impurities in semiconductors. We note that the dependence of the relaxation transition probability on the plasma frequency Ω makes it possible, in principle, to determine this frequency from measurements of the relaxation time. It is thus possible, by using impurity ions as "paramagnetic probes," to obtain the characteristics of a solid-state plasma. If the carrier density in the sample is known (for example, from independent experiments), then the effective masses of these carriers can be regarded as the sought quantities. Even the fact that a possibility exists of determining both the plasma parameters and the characteristics of the semiconductor band structure makes the performance of the appropriate experiments desirable.

1)The results can be easily generalized to include a two-component carrier plasma.

2)The efficiency of the relaxation mechanisms based on the interaction of the impurity-center spin with the fluctuating magnetic fields of the plasma is of the same order.

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