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THEORY OF RELAXATION IN INHOMOGENEOUSLY BROADENED EPR LINES

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Relaxation processes in inhomogeneously broadened EPR lines are studied in detail by a quantum statistical method with allowance for the spatial distribution of the spins and the variation of the mean energy of the dipole-dipole interactions. It is shown that, for the case of appreciable inhomogeneous broadening, the latter does not introduce changes in the technique for deriving the probability density function for cross-relaxational transitions and does not affect the form of the relaxational curves.

1. INTRODUCTION

A theory of relaxation in inhomogeneously broadened EPR lines with allowance for spectral diffusion was developed in[1]. Relaxation curves were obtained which depended on the form,,with respect to the frequency, of the probability density function $w(\omega)$ for cross-relaxational transitions and it was established that these curves have a non-exponential character, in good agreement with experimental data. The basic equation was of a phenomenological nature and was obtained on the basis of the theory of cross-relaxation developed in the papers of Bloembergen et al.[2] and of Portis[3] [1]. The use of this equation has turned out to be extremely fruitful, since it has been possible, on the basis of this equation and with certain additional assumptions, to develop a technique for deriving the function $w(\omega)$, which characterizes the efficiency of energy absorption by the dipole-dipole "reservoir," from experimental data. However, inasmuch as the question of the spatial distribution of the spins, which can substantially affect the function $w(\omega)$, was not considered, the physical meaning of this function remained not completely clear.

The aim of this work is a more detailed and systematic treatment of relaxation in inhomogeneous broadened lines with allowance for variation in the mean energy of the dipole-dipole interactions and for the spatial distribution of the spins. Such an approach makes it possible to obtain more complete information on relaxation processes in magnetically dilute crystals.

To elucidate the quantum statistical meaning of the function $w(\omega)$, we shall obtain an equation analogous to (2) from[1], starting from the equation of motion for the density matrix. The method for obtaining the kinetic equations was developed by Provotorov et al.[5-7] We shall generalize the equations of[6] (obtained for a system consisting of spins of two types) to the case of a large number of spin packets forming an inhomogeneous EPR line. We remark that an equation analogous to the one we investigate below was used in[8,9] to analyze stationary saturation in inhomogeneously broadened lines. However, the systematic quantum-statistical derivation of such an equation is of interest in its own right for the determination of the range of applicability of the integro-differential equation describing the process of relaxation of inhomogeneously broadened lines.

As in[1], we shall use Portis' model of spin packets. Some authors criticize this model[10] on the grounds of the difficulties in the precise definition of the concept of a spin packet. However, the investigations of Khutsishvili et al.[8,11] have shown that many experimental data on the saturation of inhomogeneous lines can be well explained in the framework of this model.

2. KINETIC EQUATIONS FOR AN INHOMOGENEOUS LINE

We shall consider processes associated with cross-relaxation in an inhomogeneous line consisting of a large number of spin packets of width $\sim T_2^{-1} \ll T_{12}$, where T_{12} is a time characteristic of the spectral diffusion, the order of which will be determined below. We assume that $T_2^{-1} \ll \Delta\Omega$ ($\Delta\Omega$ is the width of the inhomogeneous line) and $\hbar\omega_0 \ll kT_0$ (ω_0 is the central resonance frequency and T_0 is the temperature of the lattice).

The equation for the density matrix of the spin system after the latter's subjection to an external perturbation (e.g., saturation) has the form

$$\frac{\partial\rho}{\partial t} = -\frac{i}{\hbar}\Big[\hat{H} + \hat{H}_{dip} + \sum_{k=0;\,1;\,2} \hat{H}_{dip}^{(k)}, \rho(t)\Big]. \tag{1}$$

Here $\hat{H} = -\hbar\sum\limits_i \omega_i S_{zi}$, $\hat{S}_{zi}$ is the operator of the z-component of the spin at the i-th lattice site, and $\omega_i = g_i\beta H_{0i}/\hbar$; H_{0i} is the magnitude of the constant magnetic field at the i-th lattice site;

$$\begin{aligned} H_{dip} = \sum_{i>j} g_i g_j |r_i - r_j|^{-3} \Big\{ &(1 - 3\gamma_{ij}^2)\hat{S}_{zi}\hat{S}_{zj} \\ &+ \delta_{\omega_i\omega_j}\Big(\frac{1}{2} - \frac{3}{4}(\alpha_{ij}^2 + \beta_{ij}^2)\Big)(\hat{S}_i^+\hat{S}_j^- + \hat{S}_i^-\hat{S}_j^+)\Big\} \end{aligned} \tag{2}$$

is the secular part of the dipole-dipole interaction operator,

$$\hat{H}_{dip}^{0} = \sum_{ij}\hat{H}_{ij}^{0}, \quad \hat{H}_{ij}^{0} \sim \hat{S}_i^+\hat{S}_j^-(1 - \delta_{\omega_i\omega_j}), \tag{3}$$

and $\hat{H}_{dip}^{(k)}$ ($k = 1, 2$) are the remaining parts of the dipole-dipole interaction operator, which lead only to direct exchange between the Zeeman and dipole-dipole

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[1] An analogous equation was studied by Kiel [4], who obtained some general laws for the spectral diffusion process.

energies. We confine ourselves to the case $\Delta\Omega \ll \omega_i$, when these terms can be neglected.

This break-down of the Hamiltonian is appropriate if the spatial distribution of the spins is not correlated with their frequency distribution. In this case, the establishment of a common temperature of the whole-dipole-dipole reservoir (DDR) proceeds at approximately the same rate as the exchange of energy within the DDR of one spin packet[8]. The terms responsible for the redistribution of energy between the DDR's of different packets are those of the form $(1 - \delta_{\omega_i\omega_j})a_{ij}\hat{S}_{zi}\hat{S}_{zj}$, which commute with the Zeeman energy of the packets, but not with $\delta_{\omega_i\omega_j}b_{ij}(\hat{S}_i{}^{+}\hat{S}_j{}^{-} + \hat{S}_i{}^{-}\hat{S}_j{}^{+})$. We shall work in a representation in which $\sum \delta_{\omega_i\omega_j}\hat{S}_{iz}$ is diagonal for all ω_j and $\hat{H}_{dip}$ is diagonal. We have omitted the terms in the Hamiltonian responsible for the spin-lattice interaction; we shall take them into account in the final kinetic equations.

Calculations analogous to those performed in[5,6] lead to the following expression:

$$\rho_1(t+\tau)-\rho_1(t) = -\frac{1}{\hbar^2}\sum_{ij}\sum_{kl}\int_t^{t+\tau}dt''\int_0^{t''}dt'\int_{-\infty}^{\infty}d\omega''\int_{-\infty}^{\infty}d\omega'$$
$$\times\{e^{i\omega''t''}e^{i\omega't'}\hat{P}'[(\hat{H}_{ij}{}^0)_{\omega''}[(\hat{H}_{kl}{}^0)_{\omega'},\rho_1(t')]]\}. \tag{4}$$

Here

$$(\hat{H}_{kl})_{\Delta\omega} = \int_{-\infty}^{\infty}\exp\left(\frac{i}{\hbar}t\hat{H}_{dip}\right)\hat{H}_{kl}{}^0\exp\left(-\frac{i}{\hbar}t\hat{H}_{dip}\right)e^{-i\Delta\omega t}\,dt, \tag{5}$$

and $\hat{p}'$ is an operator which picks out the diagonal parts of the operator following it; ρ_1 is the density matrix in the interaction picture.

We note that the double commutators in (4) are nonzero only in three cases:

1) $l=i;\quad k=j,\quad$ 2) $l=i;\quad j\neq k,\quad$ 3) $k=j;\quad i\neq l.$

In the first case we obtain

$$\left(\frac{\partial\rho_1}{\partial t}\right)_1 = -\sum_{ij}\frac{\pi}{\hbar^2}\hat{P}'[(\hat{H}_{ij}{}^0)_{-\Delta_{ij}}[(\hat{H}_{ij}{}^0)_{\Delta_{ij}},\rho_1(t)]]. \tag{6}$$

In the second case we have

$$(\rho_1(t+\tau)-\rho_1(t))_2 = -\frac{1}{\hbar^2}\sum_{ijk}\int_t^{t+\tau}dt''\int_0^{t''}dt'\int_{-\infty}^{\infty}d\omega''\{e^{i\omega''(t''-t')}$$
$$\times e^{it''\Delta_{ij}}e^{-it'\Delta_{ik}}\hat{P}'[(\hat{H}_{ij}{}^0)_{\omega''}[(\hat{H}_{ki}{}^0)_{-\omega''},\rho_1(t')]]\}. \tag{7}$$

After integration over t', the factor in front of the double commutator takes the form

$$\exp\{i(\Delta_{ij}-\Delta_{ik})t''\}(-1+\exp\{i(\omega''+\Delta_{ik})t''\})/i(\omega''+\Delta_{ik}).$$

According to case (3), the j-th and k-th spins belong to different spin packets. We shall assume that in this case $|\Delta_{ij} - \Delta_{ik}| \gtrsim 1/\Delta T_0 \ll T_{12}$. Physically, this assumption means that there is small probability of finding two spins, differing in their resonance frequencies by $|\Delta_{kj}| < 1/\Delta t_0$, at a distance at which the dipole-dipole interaction is effective. The average value of the quantity $|\Delta_{kj}|$, $k \neq j$, can be estimated from the relation $\Delta\Omega/N(i) = \Delta_{av}$, where $N(i)$ is the number of particles effectively interacting with the i-th. We choose τ such that $\Delta t_0 \ll \tau \ll T_{12}$. Then the corresponding terms in (7) are small because of the factor $\exp\{i(\Delta_{ij} - \Delta_{ik})t''\}$ which oscillates rapidly in time (they are of order $\Delta t_0\tau^{-1}$ relative to the other terms); they can therefore be neglected. The condition $\tau \ll T_{12}$ is necessary for it to be possible to put $\rho_1(t+\tau) - \rho_1(t) \approx \tau\partial\rho_1/\partial t$. Physically, this means that we are choosing a time-scale τ such that it smooths out processes associated with improbable distributions of strongly interacting spins but is small compared with the characteristic cross-relaxation times. In addition, it is necessary that processes within one spin packet be smoothed out, i.e., that $T_2 \ll \tau$.

The case $k = j$, $i \neq l$ is investigated analogously.

In obtaining the kinetic equation for the density matrix, we have neglected its off-diagonal elements. It follows from the work of Provotorov[6] that this is justified if $(\mu H_{loc}\Delta t_0/\hbar)^2 \ll 1$. Besides, as we have seen, the conditions

$$T_2 \ll T_{12},\qquad \Delta t_0 \ll T_{12}.$$

are important for us. With these assumptions, we obtain the final equation:

$$\frac{\partial\rho_1(t)}{\partial t} = -\frac{\pi}{\hbar^2}\sum_{ij}\hat{P}'[(\hat{H}_{ij}{}^0)_{-\Delta_{ij}}[(\hat{H}_{ji}{}^0)_{\Delta_{ij}},\rho_1(t)]]. \tag{8}$$

As was shown in[5,6], for $T_{12} \gg \hbar/\mu H_{loc}$ the system can be characterized at any moment of time by the equilibrium density matrix:

$$\rho_1(t) = C\exp\Big\{\sum_l\alpha_l(t)\hat{S}_{zl} + \gamma(t)\hat{H}_{dip}\Big\}. \tag{9}$$

The quantity C is determined from the normalization condition $\mathrm{Tr}\,\rho_1 = 1$; $C = (2S+1)^{-N}$, where N is the total number of spins in the sample. Calculations of the average values $\langle\partial S_{zi}/\partial t\rangle$ and $\langle\partial H_{dip}/\partial t\rangle$ lead to the following equations for the coefficients α_i and γ:

$$\frac{\partial\alpha_i(t)}{\partial t} = -\sum_k W_{ik}(\alpha_i(t)-\alpha_k(t)-\hbar\Delta_{ik}\gamma(t)), \tag{10a}$$

$$\frac{\partial\gamma(t)}{\partial t} = \sum_{ij}V_{ij}\hbar\Delta_{ij}(\alpha_i(t)-\alpha_j(t)-\hbar\Delta_{ij}\gamma(t)), \tag{10b}$$

where

$$W_{ik} = \frac{2\pi}{\hbar^2}\frac{\mathrm{Sp}\,\hat{P}'(\hat{H}^0_{ik})_{-\Delta_{ik}}(\hat{H}^0_{ki})_{\Delta_{ik}}}{\mathrm{Sp}\,\hat{S}^2_{zi}}, \tag{11}$$

$$V_{ik} = \frac{\mathrm{Sp}\,\hat{S}_{iz}{}^2}{\mathrm{Sp}\,\hat{H}^2_{dip}}W_{ik}. \tag{12}$$

Now we can determine the order of magnitude of T_{12} and T'_{12}:

$$1/T_{12} \approx (W_{ik})_{av},\qquad 1/T_{12}{}' \approx (V_{ik})_{av}. \tag{13}$$

The treatment given above is valid if it can be assumed that the spins belonging to one spin packet are quantized independently. If this is not the case, calculations show that terms will occur in the kinetic equation which are quadratic in the concentration and are determined by correlation functions of the form $\langle S_i^+(t')S_k{}^-(t')S_i{}^-(t'')S_l{}^+(t'')\rangle$.

In the right-hand side of Eq. (10a) we separate out the terms referring to the m-th spin packet (characterized by a resonance frequency ω_m) and rewrite it in the form

$$\sum_m\Big\{\sum_k^{(m)}W_{ik}\Big)(\alpha_m(t)-\alpha_i(t)+\hbar\Delta_{ij}\gamma(t))\Big\}. \tag{14}$$

Here the index m indicates summation over the spins of the m-th spin packet; this summation is performed in practice over the spacings between the spin i and the spins belonging to the m-th packet. One can write

$$\sum_k^{(m)} W_{ik} = n(\omega_m)\,w(\omega_m, \omega_i) = \frac{n(\omega_m)\,w'(\omega_m - \omega_i)}{r_e^3(\omega_m, \omega_i)}, \tag{15}$$

where $n(\omega_i)$ is the number of spins per unit volume in the i-th spin packet and the factor $1/r_e^\varepsilon$ characterizes the correlation between the spatial and frequency distributions of the spins. Eq. (10a) takes the form

$$\frac{\partial \alpha_i(t)}{\partial t} = \sum n(\omega_m)\,w(\omega_m, \omega_i)\,[\alpha_m(t) - \alpha_i(t) + \hbar\Delta_{im}\gamma(t)]. \tag{16}$$

Let the line broadening be associated only with the inhomogeneity of the g-factor, so that there is no special correlation between the position of a spin and its frequency. Then the probability that the distance between two arbitrary spins, for sufficiently dilute systems, lies in the interval r to r + dr can be determined from Hertz's formula[12]:

$$dW(r) = \exp\left(-\frac{4\pi}{3}r^3 n\right)4\pi r^2\,dr, \tag{17}$$

where n is the number of paramagnetic ions per unit volume. In our case, we have

$$\sum_k^{(m)} W_{ik} \approx n(\omega_m)\int_{r_0}^{\infty}\frac{a^2(\omega_r)}{r^6}\exp\left(-\frac{4\pi r^3}{3}n(\omega_m)\right)4\pi r^2\,dr. \tag{17a}$$

In this formula the distances are reckoned from the i-th spin; r_0 is the distance between the closest lattice sites able to be occupied by paramagnetic ions; $a^2(\omega_r)/r^6$ are the squares of the corresponding matrix elements of the dipole-dipole interaction operator, g given by expression (11). The absence of correlation between the spatial and spectral spin distributions means that $a^2(\omega_r) = w''(\omega_m - \omega_i)$, and we obtain the following result

$$\sum_k^{(m)} W_{ik} \approx \frac{4\pi}{3}n(\omega_m)\,w''(\omega_m - \omega_i)\int_{r_0^3}^{\infty}\frac{1}{\xi^2}\exp\left(-\frac{4\pi}{3}n(\omega_m)\xi\right)d\xi. \tag{17b}$$

It follows from this formula that, for not too small concentrations, we cannot obtain, generally speaking, an equation of the type used, e.g., in[1,2,4]. The dependence on the concentration of paramagnetic ions in the terms of the right-hand side of the equation can, in principle, be non-linear, and, for very small concentrations only, when we can confine ourselves to the linear term, we obtain

$$\sum_k^{(m)} W_{ik} \approx \frac{4\pi}{3}n(\omega_m)\,w''(\omega_m - \omega_i)\frac{1}{r_0^3} = n(\omega_m)\,w'(\omega_m - \omega_i)\frac{1}{r_0^3}. \tag{18}$$

A comparison of Eqs. (15), (17a), (17b) and (18) shows that, in the case of a random spatial distribution of spins with different resonance frequencies, the quantity r_e is determined by the equality

$$\frac{1}{r_e^3(\omega')} = \int_{r_0^3}\frac{1}{\xi^2}\exp\left(-\frac{4\pi}{3}n(\omega')\xi\right)d\xi, \tag{19a}$$

or, for small concentrations of paramagnetic impurity,

$$r_e \approx r_0. \tag{19b}$$

If in the derivation of the function $w(\omega)$ it is found that $1/r_e^3 > 1/r_0^3$, this will mean that there exist some clusters of spins with close frequencies; however, if $1/r_e^3 < 1/r_0^3$, the spatial clusters contain spins with a large spread of resonance frequencies. Comparison of r_e and r_0 makes it possible to estimate the dimensions of the above-mentioned clusters.

To pass over to a continuous distribution of spin packets, we note that for our case the condition $\mu H_{\text{loc}}/\hbar\Delta_{ij} \ll 1$ can be written in the form

$$\mu^2/r_{ij}^3\Delta_{ij} \ll 1. \tag{20a}$$

Thus, we confine ourselves to the case when there is small probability of close spacing of two spins characterized by close resonance frequencies. In the absence of any special correlation between the spatial and frequency distributions of the spins in crystals with a small paramagnetic impurity concentration and a large spread of frequencies (i.e., with significant inhomogeneous linewidth), this assumption is fully justified. To assess the applicability of this theory, we can use the relation

$$\mu^2/r_{\text{eff}}^3\Delta_{\text{av}} \ll 1, \tag{20b}$$

where $1/r_{\text{eff}}^3 = \langle 1/r^3\rangle$ and the averaging is performed over the distribution (17).

The terms describing the spin-lattice relaxation can be obtained analogously. We shall assume that the spin-lattice relaxation time T_1 is constant over the width of the inhomogeneous line (cf.[1]).

As in[1], we pass on to a spin packet distribution which is quasi-continuous in frequency; then Eq. (16) and the analogous equation for $\langle H_{\text{dip}}(t)\rangle$ will take the form ($\alpha_i - \alpha_{i0} \to u_1(x, t)$, and x is the frequency detuning relative to the central component of the line):

$$\frac{\partial u_1(x,t)}{\partial t} = \int_{-\infty}^{\infty} w(x - x')\,n(x')\,[u_1(x',t) - u_1(x,t)$$

$$+ (x' - x)\,g(t)]\,dx' - u_1(x,t)/T_1, \tag{21a}$$

$$\frac{dg(t)}{dt} = \hbar^2\lambda\int\!\!\int dx\,dx'\{(x' - x)\,w(x' - x)\,n(x')\,n(x)\,[u_1(x,t)$$

$$- u_1(x',t) - (x' - x)\,g(t)]\} + \frac{g - g_0}{T_1'}. \tag{21b}$$

Here α_{i0} is the equilibrium value of $\alpha_i(t)$; $g(t) = \hbar\gamma(t)$, $\lambda = \text{Tr}\,\hat{S}_{zi}^2/\text{Tr}\,\hat{H}_{\text{dip}}^2$, g_0 is the equilibrium value of g(t), and T_1' is the spin-lattice relaxation time for $H_{\text{dip}}(t)$.

3. STUDY OF THE KINETIC EQUATIONS

We shall analyze the system of Eqs. (21) which we have obtained.

1. We define $f(t) = \int_{-\infty}^{\infty} u_1(x, t)\,n(x)\,dx$, multiply Eq. (21a) by n(x) and integrate it over x. Then $\partial f(t)/\partial t = -f(t)/T_1$. Consequently, the area under the curve which describes the "hole" in the imhomogeneous line relaxes exponentially with a time T_1. (The function $u(x, t) = n(x)\,u_1(x, t)$ in fact describes the shape of the "hole.") Here and below, we shall assume the functions n(x) and w(x) to be symmetric with respect to the central component ω_0; this is in any case justified, as we have explained, for a random paramagnetic impurity distribution.

2. We turn to the second equation. We shall consider the integral

$$I = \int\!\!\int dx\,dx'\,(x' - x)\,w(x - x')\,n(x)\,n(x')\,[u_1(x) - u_1(x')].$$

If $n(x)$ varies slowly in comparison with $w(x)$ (if $w(x)$ falls off at spectral distances of order Δx_0, our assumption means that $\Delta x_0 \ll \Delta\Omega$), then this integral is equal to zero in the zeroth approximation, while the first correction gives

$$I = 2M_2 h(t), \tag{22}$$

where

$$M_2 = \int z^2 w(z)\,dz, \qquad h(t) = \int dx \frac{dn}{dx} u(x, t).$$

Thus, in the zeroth approximation,

$$\frac{dg(t)}{dt} = -\hbar^2\lambda g(t) \iint dx\,dx' n(x) n(x')(x - x')^2 w(x - x') + \frac{g - g_0}{T_1'} \approx -\hbar^2\lambda g(t) M_2 K + \frac{(g - g_0)}{T_1'}, \qquad K = \int n^2(x)\,dx. \tag{23}$$

Since the function $h(t)$ is determined from observed curves, one can also find the relaxation curve with allowance for the first correction.

3. We return to Eq. (21a). We rewrite it in the form

$$\frac{\partial u(x, t)}{\partial t} = -\frac{u(x, t)}{T_1} + \int_{-\infty}^{\infty} w(x - x')[n(x)u(x') - n(x')u(x) + n(x)n(x')(x' - x)g(t)]\,dx'. \tag{24}$$

We note that the integral $\int (x - x')n(x)n(x')w(x - x')dx'$ is close to zero if $\Delta x_0 \ll \Delta\Omega$. This means that for strongly inhomogeneously broadened lines the correction associated with the change in the average energy of the dipole interactions turns out to be unimportant, if the prior saturation process does not give rise to any sharp change in the temperature of the dipole-dipole reservoir ($u/\omega_0 \sim g$). In[1] it was shown that for the Nd^{3+} line in a monocrystal of fluoroapatite this condition is well fulfilled. We shall assume, in addition, that the "hole" width $\Delta\omega_0 \ll \Delta\Omega$[2)]. Then

$$\int w(x - x')n(x)u(x')\,dx' \approx \int w(x - x')n(x - x')u(x')\,dx',$$

$$\int w(x - x')n(x')u(x)\,dx' \approx u(x) \int w(x - x')n(x - x')\,dx' = u(x)/T_\Sigma \tag{25}$$

(T_Σ is a certain parameter characterizing the cross-relaxation). Let $w(x)n(x) = W(x)$. We Fourier-transform Eq. (24), taking the relations (25) into account (the tilde denotes the Fourier transform):

$$\frac{\partial \tilde{u}(y, t)}{\partial t} = -\tilde{u}(y, t)\left[\frac{1}{T_1} + \frac{1}{T_\Sigma} - \sqrt{2\pi}\tilde{W}(y)\right].$$

This equation is analogous to that obtained in[1]. By the technique indicated there, we can derive the functions $W(x)$ and $w(x)$, and, using (23), indirectly determine the characteristic time T'_{12} for the cross-relaxation $H_{dip}(t)$.

In ordinary conditions it will not be justified to take account of the term in Eq. (24) containing $g(t)$, since the corrections associated with it correspond in order of magnitude to additional effects arising from the falling off of the function $n(x)$. Therefore, for a more exact determination, one must try to obtain as narrow a "hole" as possible.

If it is necessary to take the line shape into account, to derive the function $w(x)$ we can make use of the technique described in the Appendix to[1]; then we shall again have the possibility of finding the cross-relaxation time for $H_{dip}(t)$.

In the case when $\Delta x_0 \gg \Delta\omega_0$ ($\Delta\omega_0$ is the "hole" width),

$$\int w(x - x')n(x')u_1(x', t)\,dx' \approx w(x) \int_{-\infty}^{\infty} u(x', t)\,dx',$$

$$u_1(x, t) \int_{-\infty}^{\infty} w(x')n(x')\,dx' = \frac{u_1(x, t)}{T_\Sigma}.$$

We define $S_0 = \int_{-\infty}^{\infty} u(y, 0)\,dy$. Since the function $f(t) = \int_{-\infty}^{\infty} u(x', t)\,dx'$ falls off like $f = -S_0 e^{-t/T_1}$, our equation takes the form

$$\frac{\partial u_1(x, t)}{\partial t} = u_1(x, t)\left(\frac{1}{T_1} + \frac{1}{T_\Sigma}\right) - w(x) S_0 e^{-t/T_1}.$$

The solution will be

$$u_1(x, t) = \exp\left\{-t\left(\frac{1}{T_1} + \frac{1}{T_\Sigma}\right)\right\}[u_1(x, 0) - T_\Sigma S_0 w(x)(e^{t/T_\Sigma} - 1)].$$

Hence it can be seen that if $T_\Sigma S_0 w(x) \ll u_1(x, 0)$, the "holes" vanish in a time $\sim T_\Sigma$. This result, possibly, is one of the reasons for the rapid disappearance of the subsidiary narrow "holes" observed in experiments on discrete saturation[13].

It is of interest to consider the case of broadening of an initially homogeneous line as a result of the inhomogeneity of an external constant magnetic field. In this case, generally speaking, one must take account of the DDR of the separate packets and of the transfer of energy betweeen them. However, if $\Delta x_0 \ll \Delta\Omega$, the change in the average energy of the dipole-dipole interactions has, as we have explained, no effect on the solution of Eq. (21a), and the function $w(\omega)$ can be derived.

We have (analogously to (15)—(17))

$$\sum_k W_{ik} \approx \int_0^\pi \sin\theta\,d\theta \int_0^{2\pi} d\varphi \int_0^\infty \frac{a^2}{r^6} n(\omega_r) w(\omega_r - \omega_i) \times \exp\left\{-\frac{4\pi r^3}{3} n(\omega_r)\right\} r^2\,dr, \qquad n(\omega_r) = \begin{cases} 0, & r < r_0, \\ \approx n = \text{const}, & r > r_0, \end{cases}$$

Let the crystal be homogeneous, and the magnetic field such that

$$\frac{\partial\omega}{\partial z} = D = \text{const}, \qquad \frac{\partial\omega}{\partial x} = \frac{\partial\omega}{\partial y} = 0,$$

i.e., the xy-plane is perpendicular to the axis along which the constant field varies. Then

$$\sum_k W_{ik} \approx \int_{-\infty}^{\infty} \frac{\pi}{2} n(\omega - \omega_i) \frac{a^2 D^3}{(\omega - \omega_i)^4} w(\omega - \omega_i)\,d\omega \tag{26}$$

in the approximation linear in the impurity concentration[3)]. We note that the function $n(\omega - \omega_i)$ in fact regularizes the integral when $\omega \to \omega_i$, inasmuch as $n(\omega - \omega_i) = 0$, if $|\omega - \omega_i| < \omega_{min}$, where $\omega_{min} \gtrsim r_0 D$. The quantity ω_{min} should be chosen in such a way that the relation $\omega_{min} > (\Delta t_0)^{-1}$ is fulfilled (cf. above); in this case, naturally, the construction of the function $w(\omega)$ is carried out accurate to quantities

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[2)] In this case we can always neglect the last term in Eq. (24), and the condition $u/\omega \sim g$ turns out to be superfluous.

[3)] Another possible treatment is to formally divide the crystal into layers of thickness $\Delta z \approx D^{-1}T_2^{-1}$ and study the exchange of energy between these layers.

$\sim\omega_{\min}$. We denote the integrand in (26) by $w^*(\omega)$. Then in place of Eq. (21a) we obtain

$$\frac{\partial u(x,t)}{\partial t}=-\frac{u(x,t)}{T_1}+\int_{-\infty}^{\infty} w^*(x-x')\,[u(x',t)-u(x,t)]\,dx'. \qquad (27)$$

It is clear that a derivation of the characteristic function $w(\omega)$ is possible only for extremely high gradients of the constant field. Otherwise, the behavior of $w^*(\omega)$ will be principally determined by the factor $1/|\omega-\omega_i|^3$.

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