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Suppression of magnetic broadening of the optical impurity absorption line by polarized pulses

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Abstract. The problem of narrowing of the homogeneous linewidth of optical impurity absorption due to the dipole–dipole interactions of magnetic moments of impurity paramagnetic ions is considered.

For this purpose the use of a coherent optical pulse sequence with different polarization directions is suggested. The conditions are obtained under which the above-mentioned method can be effective.

Optical spectroscopy provides extensive information on the relaxation and spectroscopic characteristics of the optical impurity absorption line in solids. In this case, however, some of the information is lost owing to the finite linewidth of optical spectra. This makes the problem of optical-absorption line narrowing very acute. The application of physical methods of line-broadening suppression becomes very important together with improvement in the experimental equipment. The removal of an inhomogeneous linewidth, usually caused by inhomogeneity of the intracrystal electric field, is achieved by various methods, e.g. by non-stationary techniques [1]. Homogeneous line broadening can be due to such factors as:

(1) a natural level width,
(2) interaction with lattice phonons,
(3) pseudo-electric dipole–dipole interactions and
(4) magnetic dipole-dipole interactions.

If the impurity absorption spectrum is investigated in the transition region with a fairly small oscillator force, the contributions of the first and third factors to the homogeneous linewidth appear to be insignificant. As for the interactions with phonons, they are suppressed by decreasing the temperature of the sample. If the contribution of pseudo-electric dipole–dipole interactions to the optical linewidth is the most significant, coherent optical pulse sequences become effective for line narrowing [2, 3].

As factors (1)–(3) of broadening are not essential, homogeneous optical linewidth will be determined by magnetic dipole–dipole interactions. This line-broadening mechanism of light impurity absorption is demonstrated especially vividly if a sample is placed in a magnetic field. The character of the broadening depends on the ion concentration. At low impurity centre concentrations the resonance flip–flop transitions of nuclear spins surrounding the ion create a fluctuating magnetic field, which substantially broadens the optical transition line of this ion. In this case, for line narrowing, a strong variable RF

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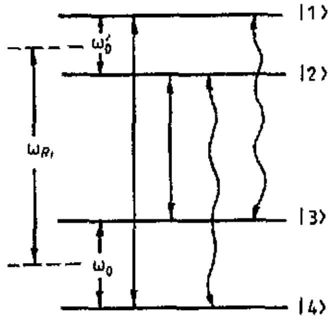

Figure 1. $|3\rangle$ and $|4\rangle$ are magnetic sublevels of the ion's ground state, and $|1\rangle$ and $|2\rangle$ are magnetic sublevels of the ion's excited state. The straight lines represent transitions induced by circularly polarized light in the XOY plane, while the wavy lines show those induced by linearly polarized light along the OZ axis.

field was used in [4], inducing nuclear spin rotation at the 'magic angle' ($\vartheta \simeq 54°$) about the constant external magnetic field. At high ion concentrations the main contribution to the homogeneous optical linewidth will be made by dipole–dipole interactions of magnetic moments of electronic shells of impurity paramagnetic ions. A number of studies on the methods of suppression of these interactions have also been published. In [5], for example, incoherent saturation of the ion optical absorption line was used, inducing transitions from a ground to an excited state with much weaker magnetic interaction constants, and in [1, 3] the narrowing of the magnetic dipole linewidth by RF pulse sequences resonant on electronic sublevel splitting in the magnetic field was suggested. In the present paper, coherent polarized optical multiple pulse sequences are also shown to be effective for averaging magnetic dipole–dipole interactions.

Let us consider a sample containing paramagnetic ions, placed in a strong constant magnetic field $\boldsymbol{H}_0 \parallel OZ$. Let us assume that the ground and excited states of each impurity centre are split into two magnetic sublevels with different g-factors and that the ion concentration in the sample is fairly high. The energy levels of this ith ion are shown in figure 1.

To describe the system under consideration let us use fictitious $\frac{1}{2}$ spin operators [6] determined as follows:

$$\begin{aligned}
&\langle \kappa | R^z_{nm} | l \rangle = \tfrac{1}{2}(\delta_{kn}\delta_{ln} - \delta_{km}\delta_{lm})\\
&\langle \kappa | R^x_{nm} | l \rangle = \tfrac{1}{2}(\delta_{kn}\delta_{lm} + \delta_{km}\delta_{ln})\\
&\langle \kappa | R^y_{nm} | l \rangle = \tfrac{1}{2}\mathrm{i}(-\delta_{kn}\delta_{lm} + \delta_{km}\delta_{ln})\\
&k, l, m, n = 1, 2, 3, 4.
\end{aligned} \tag{1}$$

In these operators the two-level ion Hamiltonian including the Zeeman Hamiltonian in the constant magnetic field $\boldsymbol{H}_0$ and the secular part of the magnetic dipole–dipole interaction (the linewidth is known to be determined by the time-dependent secular part of the dipole–dipole interaction) is written as follows (the system of units where $\hbar = 1$ is used here):

$$\mathcal{H}_Z = \sum_i [\omega_{Ri}(R^{zi}_{14} + R^{zi}_{23}) + \omega_0 R^{zi}_{34} + \omega_0' R^{zi}_{12}] \tag{2}$$

$$\mathcal{H}_{dd} = \sum_{i<j} U_{ij}[3R^{zi}_{34}R^{zj}_{34} - (\boldsymbol{R}^i_{34} \cdot \boldsymbol{R}^j_{34})]. \tag{3}$$

Here ω_{Ri} is the energy of the optical transition of the ith ion, ω_0 and ω_0' are the magnetic Zeeman frequencies of the ground and excited states, respectively, of the paramagnetic ion, and $U_{ij} = \frac{1}{4}g^2\beta^2(1 - 3\cos^2\theta_{ij})/r_{ij}^3$(where β represents the Bohr magneton, $\boldsymbol{r}_{ij}$ represents the vector which connects the i and j spins, and θ_{ij} is the angle between $\boldsymbol{r}_{ij}$ and $\boldsymbol{H}_0$). Ion ground-state sublevels are predominantly occupied and hence the dipole–dipole interaction involving ions in excited states is ignored.

In the dipole approximation the ion–light interaction operator V is $V = -\boldsymbol{d}\cdot\boldsymbol{E}$, where $\boldsymbol{d}$ represents the ion dipole moment operator and $\boldsymbol{E} = 2\boldsymbol{E}_0\cos(\omega t - \boldsymbol{\kappa}\cdot\boldsymbol{r} + \phi_0)$ is the electrical component of a light wave ($\boldsymbol{k}$ is the wavevector, ω is the light frequency, and ϕ_0 is the initial phase). For the ion concentration, when the dipole–dipole interaction still contributes significantly to the optical impurity absorption line broadening the average impurity centre distance r_{ij} is considerably smaller than the light wavelength. Consequently the $\boldsymbol{k}\cdot\boldsymbol{r}$ phase can be taken to be the same for both the ith and the jth ion and is included in the initial phase ϕ_0.

Let us assume that owing to the selection rules the transitions $1 \leftrightarrows 3$ and $2 \leftrightarrows 4$ are induced by the light linearly polarized along the OZ axis, and the transitions $1 \leftrightarrows 4$ and $2 \rightleftarrows 3$ are induced by the circularly polarized light. In this case with the use of operators of fictitious spins the interaction V of the light with the ion for light of differently polarizations can be written as follows:

$$V_z = \Omega(R_{13}^+ - R_{24}^+)\exp[-\mathrm{i}(\omega t + \varphi)] + \Omega(R_{13}^- - R_{24}^-)\exp[\mathrm{i}(\omega t + \varphi)]$$

polarized along $OZ \parallel \boldsymbol{H}_0$

$$V_+ = \Omega R_{14}^+\exp[-\mathrm{i}(\omega t + \varphi)] + \Omega R_{14}^-\exp[\mathrm{i}(\omega t + \varphi)]$$

right circularly polarized (in the XOY plane) and

$$V_- = \Omega R_{23}^+\exp[-\mathrm{i}(\omega t + \varphi)] + \Omega R_{23}^-\exp[\mathrm{i}(\omega t + \varphi)]$$

left circularly polarized (in the XOY plane) where $R^{\pm} = R^x \pm \mathrm{i}R^y$, $R_{nm}^{\pm} = \Sigma_i R_{nm}^{\pm i}$ and $\Omega = |\boldsymbol{E}_0|\cdot|\boldsymbol{d}_{nm}|$.

Here the matrix element of the dipole moment is taken between the sublevels of ground and excited states. This matrix element is connected with the transition oscillator force and as a rule is known from the experimental data.

We use the linearly polarized light along the OX and OY axes instead of the circularly polarized light in the XOY plane. In this situation because of the phasal relationship between the right and left circularly polarized lights, V_x and V_y can be written

$$V_x = \Omega(R_{14}^+ + R_{23}^+)\exp[-\mathrm{i}(\omega t + \varphi)] + \Omega(R_{14}^- + R_{23}^-)\exp[\mathrm{i}(\omega t + \varphi)]$$

$$V_y = \Omega(R_{14}^+ - R_{23}^+)\exp[-\mathrm{i}(\omega t + \varphi)] + \Omega(R_{14}^- - R_{23}^-)\exp[\mathrm{i}(\omega t + \varphi)].$$

As will be seen below, the combined effect of two light waves with different polarization directions (e.g. along OZ and OX) on the system is of special interest. In this case the total Hamiltonian of the system is

$$\begin{aligned} H = H_Z + H_{\mathrm{dd}} &+ \Omega_1(R_{13}^+ - R_{24}^+)\exp[-\mathrm{i}(\omega_1 t + \varphi_1)] \\ &+ \Omega_1(R_{13}^- - R_{24}^-)\exp[\mathrm{i}(\omega_1 t + \varphi_1)] \\ &+ \Omega_2(R_{14}^+ - R_{23}^+)\exp[-\mathrm{i}(\omega_2 t + \varphi_2)] \\ &+ \Omega_2(R_{14}^- - R_{23}^-)\exp[\mathrm{i}(\omega_2 t + \varphi_1)]. \end{aligned} \tag{4}$$

Let us now consider the rotating frame defined by the transformation

$$U_z(t) = \exp\{-\mathrm{i}t[\bar{\omega}_R(R_{14}^z + R_{23}^z) + \omega_0 R_{34}^z + \omega_0' R_{12}^z]\}$$

where $\bar{\omega}_R$ is the central frequency of the inhomogeneously broadened line of paramagnetic ions.

In this system of axes the Hamiltonian (4) becomes

$$\mathscr{H} = \sum_i \Delta_i (R_{14}^{zi} + R_{23}^{zi}) + \mathscr{H}_{dd} + \tilde{V} \tag{5}$$

where $\Delta_i = \omega_{Ri} - \bar{\omega}_R$ and

$$\begin{aligned} \tilde{V} = \Omega_1 R_{13}^x \cos\{[\omega_1 - \bar{\omega}_R - (\omega_0' - \omega_0)/2]t + \varphi_1\} \\ + \Omega_1 R_{13}^y \sin\{[\omega_1 - \bar{\omega}_R - (\omega_0' - \omega_0)/2]t + \varphi_1\} \\ - \Omega_1 R_{24}^x \cos\{[\omega_1 - \bar{\omega}_R + (\omega_0' - \omega_0)/2]t + \varphi_1\} \\ - \Omega_1 R_{24}^y \sin\{[\omega_1 - \bar{\omega}_R + (\omega_0' - \omega_0)/2]t + \varphi_1\} \\ + \Omega_2 R_{14}^x \cos\{[\omega_2 - \bar{\omega}_R - (\omega_0' + \omega_0)/2]t + \varphi_2\} \\ + \Omega_2 R_{14}^y \sin\{[\omega_2 - \bar{\omega}_R - (\omega_0' + \omega_0)/2]t + \varphi_2\} \\ + \Omega_2 R_{23}^x \cos\{[\omega_2 - \bar{\omega}_R + (\omega_0' + \omega_0)/2]t + \varphi_2\} \\ + \Omega_2 R_{23}^y \sin\{[\omega_2 - \bar{\omega}_R + (\omega_0' + \omega_0)/2]t + \varphi_2\}. \end{aligned} \tag{6}$$

In deriving equation (6) we have taken into account the well known commutation relations between fictitious spin operators [6].

Let us use the effective Hamiltonian expression with accuracy up to the second order of the perturbation theory, obtained in [7] for a description of the combined effect of two light waves on the system:

$$V_{\text{eff}}^{(2)} = \bar{V} + \tfrac{1}{2}[\overline{\bar{\bar{V}}, V}] \tag{7}$$

where

$$\bar{V} = \lim_{T\to\infty} \left(\frac{1}{T} \int_0^T V(t)\, \mathrm{d}t \right) \tag{8}$$

$$\bar{\bar{V}} = \mathrm{i} \int^t [V(t') - \bar{V}]\, \mathrm{d}t'. \tag{9}$$

If the frequencies ω_1 and ω_2 are so different from $\bar{\omega}_R$ that $\Omega_{1,2}/|\omega_{1,2} - \bar{\omega}_R| \ll 1$, then it is seen from (7) and (8) that all the terms in (6) are averaged to zero in the first order of approximation. Now substituting equation (6) into (7) and averaging, after simple calculations we obtain the following effective interaction (which does not commute with $R_{34}^{x,y}$) in the second order of approximation:

$$\begin{aligned} V_{\text{eff}}^{(2)} = -\tfrac{1}{4}\Omega_1\Omega_2[1/(\omega_1 - \bar{\omega}_R) + 1/(\omega_2 - \bar{\omega}_R)][\![R_{34}^x\{\cos[(\omega_1 - \omega_2 - \omega_0)t + \varphi] \\ - \cos[(\omega_1 - \omega_2 + \omega_0)t + \varphi]\} + R_{34}^y\{\sin[(\omega_1 - \omega_2 - \omega_0)t + \varphi] \\ + \sin[(\omega_1 - \omega_2 + \omega_0)t + \varphi]\}]\!] \end{aligned} \tag{10}$$

where $\varphi = \varphi_1 - \varphi_2$.

Let us choose ω_1 and ω_2 so that $\omega_1 - \omega_2 = \omega_0$. Then omitting the non-resonance oscillating part $(\Omega_1\Omega_2/|\omega_{1,2} - \bar{\omega}_R|\omega_0 \ll 1)$ in (10) we obtain that in the rotating frame the system develops under the influence of the Hamiltonian

$$\mathcal{H}' = \sum_i \Delta_i (R_{14}^{zi} + R_{23}^{zi}) + \mathcal{H}_{\rm dd} - \tfrac{1}{4}\Omega_1\Omega_2\left(\frac{1}{\omega_1 - \bar{\omega}_R} + \frac{1}{\omega_2 - \bar{\omega}_R}\right) \times (R_{34}^{\xi} \cos\varphi + R_{34}^{\chi} \sin\varphi). \tag{11}$$

The last term in (11) describes the combined effect of two light waves polarized along OZ and OX in the system. If the duration $t_{\rm w}$ of these light pulses is such that

$$\tfrac{1}{4}\Omega_1\Omega_2[1/(\omega_1 - \bar{\omega}_R) + 1/(\omega_2 - \bar{\omega}_R)]t_{\rm w} = \tfrac{1}{2}\pi \tag{12}$$

then we can consider that the internal Hamiltonian of the system is affected by the pulse, which causes the 90° turning of electron spins around the OY and OX axes of the spin space determined by the operators R_{34}^{ξ} and R_{34}^{χ} of fictitious spin. Choosing the phase difference alternatively equal to 0, $\frac{1}{2}\pi$, π, $\frac{3}{2}\pi$, the corresponding Heisenberg operators of 90° pulses are

$$P_x = \exp(-\mathrm{i}\tfrac{1}{2}\pi R_{34}^{\xi}) \qquad P_{-x} = \exp(\mathrm{i}\tfrac{1}{2}\pi R_{34}^{\xi})$$
$$P_y = \exp(-\mathrm{i}\tfrac{1}{2}\pi R_{34}^{\chi}) \qquad P_{-y} = \exp(\mathrm{i}\tfrac{1}{2}\pi R_{34}^{\chi}).$$

Let us assume that the pulse length, defined by equation (12), satisfies the following condition $t_{\rm w} \ll T_1, T_2, \Delta_i^{-1}$ (T_1 and T_2 are the longitudinal and transverse relaxation times, respectively). Then relaxation and inhomogeneous effects can be neglected during the action of pulses and, similar to the case of magnetic resonance for suppression of dipole–dipole interactions of ions in the ground states, the so-called multiple pulse sequence WHH-4 [8] can be used:

$$\text{WHH-4}: (-|\tau - P_{-x} - \tau - P_y - 2\tau - P_{-y} - \tau - P_x - \tau)_n.$$

Here τ is the interval between pulses and the sequence is repeated with a period of $t_{\rm c} = 6\tau$.

Taking into account the commutation relations between fictitious operators we can easily see that in the zero order of the average Hamiltonian theory [8] the average value of $\bar{\mathcal{H}}_{\rm dd}$ over the $t_{\rm c}$ time period is

$$\bar{\mathcal{H}}_{\rm dd} = \frac{1}{t_{\rm c}}\int_0^{t_{\rm c}} \mathcal{H}_{\rm dd}(t)\,\mathrm{d}t = \frac{1}{t_{\rm c}}\sum_{i<j} U_{ij}\{2\tau[3R_{34}^{zi}R_{34}^{zj} - (\boldsymbol{R}_{34}^{i}\cdot\boldsymbol{R}_{34}^{j})] + 2\tau[3R_{34}^{yi}R_{34}^{yj} - (\boldsymbol{R}_{34}^{i}\cdot\boldsymbol{R}_{34}^{j})] + 2\tau[3R_{34}^{xi}R_{34}^{xj} - (\boldsymbol{R}_{34}^{i}\cdot\boldsymbol{R}_{34}^{j})]\} = 0.$$

From the physical point of view this means that, as a result of the effect of such pulse sequence, the spins make forced turns in the spinal space, which averages magnetic dipole–dipole interactions.

Thus under the effect of the above-mentioned sequence the secular part of the dipole–dipole interaction is averaged to zero. Here, as can be easily seen, this sequence does not result in suppression of a number of interactions (e.g. a hyperfine interaction) also contributing to the homogeneous broadening of optical absorption line.

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