Motional narrowing of EPR line in Kondo-lattice with heavy fermions

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Abstract. An additional contributions to the EPR linewidth besides the Kondo interaction are calculated for the Kondo lattice with heavy fermions YbRh$_2$Si$_2$. It is found that the broadening of the Electron Paramagnetic Resonance (EPR) line due to the usual dipole-dipole and anisotropic RKKY interactions should be much larger than the experimentally observed total EPR linewidth. It is shown that these contributions can be considerably reduced due to motional narrowing of the EPR line caused by the translational diffusion of quasi-localized $4f$-electrons.

1. Introduction
According to the common belief based on the single ion Kondo effect the EPR signal could not be observed in compound YbRh$_2$Si$_2$, since magnetic moments of the Kondo ions should be screened by conduction electrons at temperatures below the Kondo temperature $T_K = 25$ K, and the EPR linewidth is expected to be of the order of $\Delta \nu = k_B T_K / 2\pi \hbar \sim 500$ GHz. However an intensive EPR signal having a rather narrow linewidth has been found in this compound [1]. The EPR signal is highly anisotropic; both resonance frequency and the linewidth strongly depend on the magnetic field orientation with respect to the crystallographic axes. The angular dependence of the EPR $g$-factor and linewidth reflects the local properties of Yb$^{3+}$ ion in a crystal electric field [2].

An existence of the EPR signal in a heavy fermion Kondo lattice was explained recently by the formation of a collective spin mode of quasi-localized $f$-electrons and conduction electrons due to exchange coupling between them [3].

At the same time one should expect additional contributions to EPR linewidth due to the other reasons: anisotropic RKKY interactions, usual magnetic dipole-dipole interactions, crystal imperfections and so on. In this paper we calculate these contributions to the EPR linewidth and show that this type of the EPR broadening can be a subject of the well known motional narrowing due to translational mobility of the $4f$-electrons.

2. Analysis
2.1. The EPR linewidth due to spin-spin interactions and imperfections of a crystal
At first we consider the EPR line broadening due to the dipole-dipole interaction. The Hamiltonian for a system of $N$ ions having magnetic moments in the external magnetic field $H_0$ contains Zeeman and magnetic dipole-dipole interaction:

$$H = H_z + H_{dd},$$ (1)
for \( i \)-th and \( j \)-th ions dipole-dipole interaction Hamiltonian takes the form

\[
H_{dd}^{ij} = \frac{\mu_B^2}{r_{ij}^3} \left( S_{ix}S_{jx} - 3g_{ix}g_{jx} + S_{iy}S_{jy} - 3g_{iy}g_{jy} - (g_{ix}g_{jy} + g_{iy}g_{jx}) \right) \sin \theta,
\]

for magnetic field directed at the angle \( \theta \) with respect to the crystal symmetry axis. We also take into account the tetragonal symmetry and put \( g_x = g_y = g_\perp \) and \( g_z = g_\parallel \); \( S'_z \) is spin operator \( z \)-component for a new direction of axes.

Since we consider the main resonance line only we should drop all the non-diagonal terms in the Hamiltonian. We keep the terms of the form \( S'_z S'_z \) (\( S'_+ = S'_x + iS'_y \), \( S'_- = S'_x - iS'_y \)) and \( S_z S_z \) only, since they don’t change the magnetic quantum number.

After the rotation to the new quantization axes and a semi-diagonal part extraction dipole-dipole Hamiltonian takes the form (we drop the accents at \( S \) for the sake of brevity)

\[
H_{dd} = \sum_{ij} \{ A_{ij} S_i S_j + B_{ij} S_{ix} S_{jz} \}
\]

with

\[
A_{ij} = \frac{\mu_B^2}{2r_{ij}^3} \left( g_\perp^2 (3n_{ij}^2 - 1) + g_\parallel^2 (1 - 3n_{ij}^2) \sin^2 \psi - (1 - 3m_{ij}^2) g_\parallel^2 \sin^2 \psi \right),
\]

\[
B_{ij} = \frac{3 \mu_B^2}{2r_{ij}^3} \left\{ \frac{2g_\parallel^2}{3} (1 - 3n_{ij}^2) - (1 - 3m_{ij}^2) g_\parallel^2 \sin^2 \psi \right\},
\]

where \( l_{ij}, m_{ij}, n_{ij} \) are direction cosines for the line, connecting \( i \)-th and \( j \)-th ions with respect to crystallographic axis \( c \).

Here for the linewidth calculation we use the Moments method [4]. Formulas for the second and the forth moments of the line are

\[
M_2 = -\frac{\text{Sp}([S^+, H_{ml}][S^-, H_{ml}])}{\text{Sp}(S^+ S^-)}.
\]
\[ M_4 = \frac{\text{Sp}([S^+, H_{int}], [S^-, H_{int}])}{\text{Sp}(S^+ S^-)}. \]  

(10)

For dipole-dipole interaction we calculate the second moment only since the form of the line for it in a dense lattice is known to be almost Gaussian. Making calculations for the nearest neighbors inside YbRh$_2$Si$_2$ we obtain the following expression for an arbitrary direction of external magnetic field

\[ M_2 = \frac{9}{16} g_\perp^4 \mu_B^4 \left(0.672 - 2.015 \sin^2 \psi + 10.511 \sin^4 \psi\right) \frac{1}{a^6}, \]  

(11)

where \( a \) is the distance between the closest Yb-ions.

Considering the line form to be Gaussian we can estimate the linewidth by the formula

\[ \Delta H = \sqrt{M_2/g_\perp \mu_B}. \]

For YbRh$_2$Si$_2$ \( g_\parallel = 0.17, ~ g_\perp = 3.56 \) \cite{1} and the distance between the closest Yb-ions \( a = 4.007 \ \text{Å} \). For example we have \( \Delta H_{\pi/2} \approx 1160 \ \text{G} \) for \( \psi = 90^\circ \), while experimental value is \( \Delta H_{\pi/2, \exp} \approx 100 \ \text{G} \) \cite{1} (this value is obtained by an extrapolation of the experimental data for \( T \rightarrow 0 \), since we estimate the dipole-dipole interaction and its contribution does not depend on temperature). So the linewidth due to the dipole-dipole interaction occurs to be an order of magnitude larger than experimentally observed one. It means that there must be some mechanism for the EPR line narrowing.

Next we consider the exchange interaction between Yb ions via conduction electrons (RKKY interaction). RKKY interaction after projection onto the Kramers ground state \cite{3} becomes anisotropic. And anisotropic RKKY interaction unlike the isotropic one leads to additional line widening. RKKY interaction Hamiltonian has the form (in the coordinate system, where magnetic field is directed along the crystallographic axis \( c \))

\[ H_{RKKY} = \sum_{ij} \{J_{\parallel} S_i^z S_j^z + J_\perp S_i^+ S_j^-\}, \]  

(12)

and after the axes rotation (described above for dipole-dipole interaction) it takes the form similar to the form of dipole-dipole interaction (6), but with the coefficients

\[ A_{ij} = \frac{1}{2} J_{\parallel}^i J_\perp^j \sin^2 \psi + J_\perp^j \left(\frac{1}{2} + \frac{1}{2} \cos^2 \psi\right), \]  

(13)

\[ B_{ij} = J_{\parallel}^i \left(1 - \frac{3}{2} \sin^2 \psi\right) + J_\perp^j \left(-\frac{1}{2} + \frac{3}{2} \cos^2 \psi\right), \]  

(14)

where \( J_{\parallel, \perp} \) are the RKKY coupling constants and \( S_j \) is the spin-1/2 operator of \( j \)-th Yb-ion.

Applying the formulas for the second and forth moments \cite{5} to the given Hamiltonian and taking into account the fact, that \( g_\parallel \ll g_\perp, \ |A_{ij}| \approx |B_{ij}|, \) and \( S = 1/2, \) for the field directed along the crystal symmetry axis we obtain

\[ M_2 = \frac{1}{4\hbar^2} \sum_j B_{ij}^2, \]  

(15)

\[ M_4 = \frac{1}{16\hbar^4} \sum_{j \neq k} [3B_{jk}^2 B_{ji}^2 + 2B_{jk}^2 (B_{ji} - B_{ki})^2 + 2B_{jk} B_{ij} (B_{ji} - B_{ki}) + 2B_{jk} B_{jk} (B_{ji} - B_{ki})^2] + \frac{1}{8\hbar^4} \sum_j B_{ji}^4. \]  

(16)
Computations for the nearest neighbors give $M_4/M_2^2 = 8.5$. An isotropic exchange interaction usually results in a line narrowing, but here due to the high anisotropy, RKKY interaction itself contributes the EPR linewidth. As it is seen from the moments ratio (that is larger than the one for the Gaussian lineform) RKKY lineform is closer to Lorentzian than to Gaussian. Still it contributes the linewidth so there must be some narrowing mechanism.

We also consider the impact of crystal imperfections since EPR spectra are sensitive to the value and symmetry of the inner electric field produced by crystal ions. We analyze the special case of helical dislocation. In this case the Hamiltonian of an interaction between the Yb ions and lattice elastic deformations takes the form \[ H_{\text{int}} = \sum_{\alpha\beta\gamma\delta} G_{\alpha\beta\gamma\delta} \varepsilon_{\alpha\beta}(r) S^i_\gamma H^i_\delta, \] (17)

where $\varepsilon_{\alpha\beta}$ are the components of a deformation tensor and $G_{\alpha\beta\gamma\delta}$ is a tensor characterizing the spin-elastic interaction. Let us once again find the second moment of the line shape using the formula (9). For a helical dislocation and magnetic field both directed along the $z$-axis

\[ M_2 = \frac{bc^2}{32} \left\{ G_{zzzz}^2 + G_{zyzz}^2 \right\} \ln \left( \frac{1}{\pi c r_0^2} \right). \] (18)

where $c$ is a dislocation concentration, $r_0$ – the distance between spins and $b$ is a slip (Burgers) vector.

To estimate the crystal imperfections input to the EPR linewidth we need to know $G$-tenzor components. Here we consider the lowest level which is a Kramers doublet only (it is well-separated from the higher levels [3]). It splits due to addition of the excited states by magnetic field with the weight $g\mu_B H/\Delta$ [7], where $\Delta$ is the crystal field splitting. Hence additional electric field potential due to a lattice deformation can be replaced by $[7] g\mu_B H V/\Delta \sim g\mu_B H$, here $V$ is the matrix element of interaction between the ion and crystal field modulation, which appears due to the lattice deformation. So we can estimate the $G$-components to be $\sim g\mu_B$. If we put $g \approx 3.5; b, r_0 \sim 4\AA$ and $c \sim 10^9$ we obtain the linewidth $\Delta H \approx 8$ Oe. So the contribution of dislocations into the line shape is negligible.

2.2. Line narrowing

Now we consider the mechanism that can lead to the EPR line narrowing – a motional narrowing due to quasi-localized $f$-electrons translational diffusion.

To analyze the influence of electron motion over the vacant lattice sites onto the width of the EPR line, we use the Hamiltonian that contains a kinetic part, describing electron motion over the vacant lattice sites $H_{\text{kin}}$, an spin-spin interaction of magnetic moments $H_{ss}$ (here we consider the specific case of anisotropic exchange) and the energy of moments in magnetic field $H_z$.

It is convenient to write the kinetic energy using the Hubbard $X$-operators. The operator $X^p_i$ is defined on each site $i$ and describes the transitions between the states $p$ and $q$, that take three possible values $|\sigma\rangle$, $|0\rangle$ ($\sigma = \uparrow, \downarrow$): with (spin up and spin down) and without electron on the site; so the operator $X^\sigma_0$, for example, creates an electron with spin $\sigma$ on the site $i$.

So, the Hamiltonian here takes the form

\[ H = H_z + H_{\text{kin}} + H_{ss}, \] (19)

where

\[ H_{\text{kin}} = \sum_{\sigma ij} t_{ij} X^\sigma_i X^{0\sigma}_j, \] (20)
\[ H_{ss} = \sum_{\alpha\sigma ij} (A_{ij} + B_{ij})X_i^{\alpha\sigma}X_j^{\sigma\alpha} + \sum_{ij} \frac{1}{2} A_{ij} (X_i^{\uparrow\downarrow}X_j^{\downarrow\uparrow} + X_i^{\downarrow\uparrow}X_j^{\uparrow\downarrow}) \]  
(21)

and

\[ H_z = g\mu_B H_0 \sum_{\alpha i} \alpha X_i^{\alpha\alpha}. \]  
(22)

Here \( t_{ij} \) is hopping energy. We should note that in \( H_{ss} \) and \( H_z \) the summations are performed over the occupied lattice sites only.

In order to determine the second and fourth moments of the line form we use the relations (9) and (10) with \( S^+ = \sum_i X_i^{\uparrow\downarrow}, \ S^- = \sum_i X_i^{\downarrow\uparrow} \).

Using the property of the Hubbard operators, \( X_i^{pq\alpha\sigma}X_i^{rs\beta\delta} = \delta_{qr}X_i^{ps\beta\delta} \), we obtain formulas for the second and fourth moments of the line.

\[ M_2 = (1 - n_0) \sum_j B_{ij}^2 \]  
(23)

\[ M_4 = (1 - n_0) \sum_j B_{ij}^4 + 2(1 - n_0)^2 \sum_{jk} B_{ij}^2 B_{ik}^2 + 2n_0(1 - n_0) \sum_{jk} (B_{kj} - B_{ij})^2 t_{ij}^2, \]  
(24)

where \( n_0 \) is a holes concentration. Since it is convenient to sum over all the lattice sites we replace the confined sums \( \sum_{ij} \) (over the occupied sites only) by the sums \( (1 - n_0) \sum_{ij} \), taken over all the sites. Therefore the factor \( (1 - n_0) \) appears.

To estimate how much does electron motion affect the linewidth we calculate the moments for the ‘nearest neighbors’ in a flat lattice (since calculation for the next neighbors is more complicated):

\[ M_2 = 2(1 - n_0) [B_0^2 + B_1^2], \]  
(25)

\[ M_4 = 2(1 - n_0) [B_0^4 + B_1^4] + 8(1 - n_0)^2 [B_0^2 + 2B_0^2B_1^2] + 16n_0(1 - n_0) [B_0 - B_1]^2 t_0^2, \]  
(26)

where "0" denotes the nearest neighbors and "1" - the next ones.

Now we can estimate the linewidth by the formula \( \bar{\Delta H} = M_2^{3/2}/M_4^{1/2} \):

\[ \bar{\Delta H} = \frac{2(1 - n_0)B_0^3}{[B_0^4 + 4(1 - n_0)B_1^4 + 8n_0B_0^2B_1^2]^{1/2}}. \]  
(27)

Now we can estimate the line narrowing due to electron motion for the case of dipole-dipole interaction. Above we have already calculated the second moment and the linewidth \( \Delta H_{dd} \approx 1200 \text{ G} \approx 0.081 \text{ K} \) for dipole-dipole interaction. Since we can see the expression, almost similar to \( M_2 \) in front of \( t_0^2 \) in \( M_4 \) (26), we can estimate the linewidth for dipole-dipole interaction with electron motion taken into account.

Hopping energy \( t_0 \) multiplied by the number of nearest neighbors is expected to be of the order of a bandwidth. It is possible to estimate it using the data of angle-resolved photoemission experiments [8]. It has been shown in [8] that Kramers doublet energy depends on the wave vector \( k \) which allows to roughly estimate the lowest doublet bandwidth to be \( \sim 100 \text{ K} \). We take \( t_0 = 20 \text{ K} \) (since \( t_0 \) is for the one neighbor only) and \( n_0 = 0.01 \), then \( \Delta H_{dd} \approx 17 \text{ G} \), which is \( \sim 70 \) times narrower than \( \Delta H_{dd} \), and much narrower than experimentally observed value, so even \( t_0 = 20 \text{ K} \) is enough to compensate the dipole-dipole linewidth.

We should expect exchange interaction to be larger than dipole-dipole one. It’s difficult to estimate its value since \( J \) is unknown, but by the formulas we can see that it could also be narrowed by electron motion.
3. Discussion
We considered several mechanisms affecting the EPR linewidth in YbRh$_2$Si$_2$ compound. It is shown that spin-spin interactions (Yb-ions dipole-dipole interaction and anisotropic RKKY-interaction) result in the linewidth much larger than experimentally observed one. Therefore, it is obvious that some narrowing mechanism must exist.

Electron motion is only one of the possible narrowing mechanisms. We believe it might be the case for YbRh$_2$Si$_2$ since due to the $f$-electrons and conduction electrons hybridization the jumping of $f$-electrons between the nearest Yb sites appears. There are several possible line narrowing mechanisms, for example a fast reorientation of Kondo ion moments in the bottleneck regime, and it is not yet possible to determine, which one is more effective.

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