EFFECTS OF LATTICE ANHARMONICITY ON SPIN-LATTICE RELAXATION IN SOLIDS

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A derivation is given for the formulas defining the operator for the spin-lattice interaction as averaged over the orbital motion of the unpaired electron in the solid. Simple formulas are derived for the constants of the spin-lattice interaction. It is shown that the relaxation time $T_1$ of this interaction may be substantially dependent on the concentration of lattice defects at helium temperatures; approximate relations between $T_1$ and the phonon mean free path are derived.

The hamiltonian envisaged here is that corresponding to the Kronig-van Vleck spin-lattice relaxation mechanism [1] in a magnetically dilute solid:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_p + V,$$  

in which $\mathcal{H}_0$ is the hamiltonian for the orbital motion of the electron in the paramagnetic center, $\mathcal{H}_p$ is the phonon operator, and the interaction $V$ (which is treated as a perturbation) is

$$V = \mathcal{H}_{SH} + \mathcal{H}_{OH} + \mathcal{H}_{SO} + \mathcal{H}_{OP},$$

in which $\mathcal{H}_{SH} + \mathcal{H}_{OH} = \beta_0 (2S + L)H_0$, $\beta_0$ is the Bohr magneton, $H_0$ is the magnetic field, $L$ is the operator for the orbital motion of the electrons, $S$ is the operator for the total spin, $\mathcal{H}_{SO} = \lambda L S$, $\lambda$ is the fine-structure constant, and $\mathcal{H}_{OP}$ is the dynamic part of the Stark interaction between the electrons and the crystalline field, this being dependent on the electron coordinates $X$ and on the displacements $x$ of the nuclei from their equilibrium positions. The static part of the Stark interaction describes that effect for the nuclei in their equilibrium lattice positions and is included in operator $\mathcal{H}_{SO}$.

In what follows I assume that $\mathcal{H}_0$ is independent of the lattice coordinates $x$. Then the operators of (1) and (2) correspond to Van Vleck’s [1] model for the mechanism of spin-lattice relaxation. The main difference between my model and that of [1] is that the form of $\mathcal{H}_p$ is not specified in advance (we do not make the assumption made in [1], i.e., that it represents a set of harmonic oscillators).

The first step is to use (1) and (2) to find an expression for an operator dependent only on the spin and lattice coordinates, this being such as to allow us to discuss processes in a system of spins and phonons that do not alter the state of orbital motion of the electrons.

We denote by $|j\rangle$, $E_j$ and $|n\rangle$, $E_n$ the eigenfunctions and eigenvalues of $\mathcal{H}_0$ and $\mathcal{H}_p$, respectively. The eigenfunction of $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_p$ is put as

$$|j\sigma\rangle = |j\rangle |n\rangle |\sigma\rangle,$$

in which $|\sigma\rangle$ is the spin function; the eigenvalues of $\mathcal{H}_0$ are degenerate with respect to $\sigma$:

$$E_{j\sigma} = E_j + E_n,$$

Initially we assume $H_0 = 0$. Then, taking state $|j\rangle$ as nondegenerate (the static crystalline field removes the degeneracy in $L_z$ for the electronic ground state), we find that

$$\langle j\sigma | \mathcal{H}_{SO} | j'n\sigma' \rangle = 0,$$

because in this case $\langle j|L_j|j\rangle = 0$. Thus the degeneracy in $\sigma$ is not removed in the first approximation with respect to $V$. In the second approximation the splitting of the level with quantum numbers $j$ and $n$ is determined from the secular equation corresponding to the following matrix [2]:

$$\langle \sigma | V^{(2)} | \sigma' \rangle = \sum_{j'n\sigma'} \frac{\langle j\sigma | V | j'n\sigma' \rangle \langle j'n\sigma' | V | j\sigma' \rangle}{E_{jn} - E_{jn'}},$$

the summation being for those $j'$ and $n'$ for which $E_{jn} - E_{jn'} \neq 0$.

We further assume that $E_{jn} - E_{jn'} \ll E_j - E_j'$. This condition signifies smallness of the vibrational quanta.
relative to the electronic ones and may be put as
\[ \omega_D \ll \Delta, \] (7)
in which \( \omega_D \) is the Debye frequency and \( \Delta \) is the splitting of the electron term in the static crystalline field. Then (6) is put as
\[ \langle \sigma | V^{(2)} | \sigma' \rangle = \sum_{j,n'\sigma'} \left\langle \frac{j n \sigma | V \rangle | j' n' \sigma' \rangle | V \rangle | n \sigma' \rangle \right\rangle \left( 1 - \frac{E_n - E_{n'}}{E_j - E_{j'}} + \ldots \right). \] (8)

Consider the terms proportional to \( \lambda^2 \) in (9):
\[ \langle \sigma | V^{(3)} | \sigma' \rangle = \lambda^2 \sum_{j,n'\sigma'} \left\langle \frac{j n \sigma | L_S | j' n' \sigma' \rangle | L_S \rangle | n \sigma' \rangle \right\rangle \times \left( 1 - \frac{E_n - E_{n'}}{E_j - E_{j'}} + \ldots \right). \] (9)

We have in (9) that
\[ \langle j n \sigma | L_S | j' n' \sigma' \rangle = \langle j | L_a | j' \rangle \langle \sigma | S_a | \sigma' \rangle \delta_{nn'}. \]

Hence
\[ \langle \sigma | V^{(3)} | \sigma' \rangle = \lambda^2 \langle \sigma | S_a S_b \rangle \langle \sigma' \rangle \sum_{j'} \left( \frac{j | L_a | j' \rangle \langle j' | L_a \rangle | j \rangle}{E_j - E_{j'}} \right). \] (10)

But precisely the same matrix is defined by the operator
\[ \mathcal{H}_S = D_{ab} S_a S_b, \] (11)
which is a known [3] expression for the spin hamiltonian.

We put \( \mathcal{H}_{OP} \) as a power series in the nuclear displacements \( x \):
\[ \mathcal{H}_{OP} = \sum_{q=1}^{\infty} F_q(x) x^q. \] (12)

By \( x \) in (12) we mean the set of quantities \( x_{m\alpha} \), in which \( m \) is the number of the atom in the lattice and \( \alpha \) is the direction of displacement; thus, for example, the quadratic term in (12) takes the form
\[ F_2(X) x^2 = F_{2ab}^{mm'}(X) x_{m\alpha} x_{m'\beta}. \] (13)

Summation with respect to the subscripts is understood, account being taken only of nuclei \( m \) and \( m' \) that lie immediately adjacent to the paramagnetic center.

Now we consider terms in (8) that contain \( S_{OP} \) and \( \mathcal{H}_{OP} \) simultaneously:
\[ \langle \sigma | V_2^{(3)} | \sigma' \rangle = \lambda \sum_{j'} \sum_q \left( \frac{j | L_a | j' \rangle \langle j' | F_q \rangle | j \rangle}{E_j - E_{j'}} \right) \times \langle n | x^q | n \rangle \langle \sigma | S_a | \sigma' \rangle. \] (14)

The matrix of (14) may also be derived in the first approximation in perturbation theory, if we take \( \mathcal{H}_p \) as our basic hamiltonian and the operator \( \mathcal{H}_{SP} \) as the perturbation, the latter being
\[ \mathcal{H}_{SP} = A_{q} x^q S_a, \]
\[ A_{q} = \sum_{j'} \left( \frac{j | L_a | j' \rangle \langle j' | F_q \rangle | j \rangle + \langle j | F_q | j' \rangle \langle j' | L_a | j \rangle \right) / (E_j - E_{j'}). \] (15)

The terms in (8) that contain products of the matrix elements of operator \( \mathcal{H}_{OP} \) are independent of the spin variables and may be included in \( \mathcal{H}_p \).