A STUDY OF THE PARAMAGNETIC SUSCEPTIBILITY OF RARE EARTH INTERMETALLICS[1]

Štefan Zajac, Filip Pešek

Faculty of Mathematics and Physics of the Charles University, Ke Karlovu 3, 121 16 Praha 2, Czech Republic

We have studied the additional influence of conduction electrons on the paramagnetic susceptibility of interacting rare earth magnetic ions on the basis of the crystal and molecular field model and thermodynamic perturbation formalism. We have applied the derived formulae to experimental data for $TmCu_2$. We have found, that in this compound the additional influence of conduction electrons on the paramagnetic susceptibility is comparable with molecular field.

1. Theory

The diagonal elements of paramagnetic susceptibility χ_i of the system are given by:

$$\chi_i = -\frac{d^2 F}{dh_i^2} \quad , \tag{1}$$

where h_i is the static magnetic field applied in direction i, $(i = x, y, z)$. The free energy F can be written as:

$$F = -\frac{1}{\beta} \ln Z \quad , \tag{2}$$

where $Z = Tr(e^{-\beta H})$ is the partition function, $\beta = 1/kT$.
We have studied rare earth intermetallic compounds with the model Hamiltonian:

$$H = H_{CEF} + H_{mol} + H_{cond} \quad . \tag{3}$$

H_{CEF} describes the influence of crystal electric field on the magnetic ion:

$$H_{CEF} = \sum_{l,m} V_l^m O_l^m (J) \quad , \tag{4}$$

where V_l^m are the crystal field parameters and $O_l^m(J)$ are Stevens operator equivalents.

H_{mol} represents the molecular field approximation of exchange interaction between magnetic ions :

$$H_{mol} = -g\mu_B(h_i + \lambda_i M_i)J_i \quad ,$$ (5)

where g is the Lande factor, μ_B is the Bohr magneton, M_i is the magnetisation and λ_i are the molecular field constants.

The last term in (3)

$$H_{cond} = I\,J\,\vec{s} = I\,(J_x s_x + J_y s_y + J_z s_z)$$ (6)

approximately describes the additional s-f type interaction of magnetic ions with conduction electrons [1].

The eigenstates and energies of H_{CEF} can be determined exactly in the $2J + 1$ dimensional Hilbert space of magnetic ion.

H_{mol} causes the changes of these eigenstates and energies, which can be determined in a self-consistent way.

We based the calculation of the influence of H_{cond} on the thermodynamic perturbation theory [2],[3],[4]. In this formalism the partition sum Z can be expressed as:

$$Z = Z_0 <\sigma> \quad ,$$ (7)

where Z_0 is the partition function of the system described by H_0, $< ... >$ is the average value calculated with the density operator corresponding to H_0 and σ is defined by the equation:

$$e^{(-\beta H)} = e^{(-\beta H_0)}\sigma \quad .$$ (8)

Here $H = H_0 + H_{cond}$, where $H_0 = H_{CEF} + H_{mol}$. The operator σ can be expressed by the infinite operational sum:

$$\sigma(\beta) = 1 + \sum_{n=1}^{\infty} \sigma_n(\beta) \quad ,$$ (9)

where

$$\sigma_n(\beta) = (-1)^n \int_0^\beta \int_0^{\tau_1} ... \int_0^{\tau_{n-1}} H_{cond}(\tau_1)...H_{cond}(\tau_n)\, d\tau_n...d\tau_1 \quad ,$$ (10)

where

$$H_{cond}(\tau) = e^{H_0\tau} H_{cond}\, e^{-H_0\tau} \quad .$$ (11)

The thermal average $<\sigma_n>$ with the density operator of the unperturbed system can be expressed as:

$$<\sigma_n> = (-1)^n \frac{1}{\sum_{n=1}^N e^{-\beta E_n}} \sum_{k(1),...k(n)=1}^N \left(e^{-\beta E_{k(n)}} \prod_{i=1}^n <k(i)|H_{cond}|k(i+1)> \times \right.$$
$$\left. \times \int_0^\beta \int_0^{\tau_1} ... \int_0^{\tau_{n-1}} \prod_{i=1}^n e^{\tau_i(E_{k(i)} - E_{k(i+1)})} d\tau_n...d\tau_1 \right)$$ (12)

CEF and I parameters [10^{-23} J/ion]
$V_2^0 = -1.2$
$V_2^2 = -2.9$
$V_4^0 = 1.7\ 10^{-2}$
$V_4^2 = -3.3\ 10^{-2}$
$V_4^4 = 3.2\ 10^{-2}$
$V_6^0 = 2.1\ 10^{-5}$
$V_6^2 = -1.3\ 10^{-3}$
$V_6^4 = 2.1\ 10^{-3}$
$V_6^6 = 5.4\ 10^{-4}$
$I = 2.9$

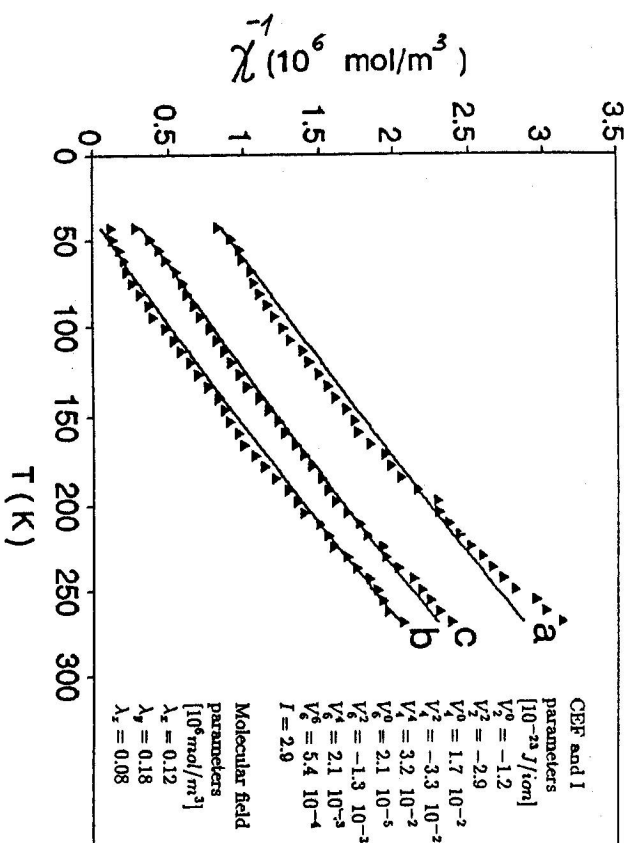| Molecular field parameters [10^6 mol/m^3] |
| --- |
| $\lambda_x = 0.12$ |
| $\lambda_y = 0.18$ |
| $\lambda_z = 0.08$ |

Fig.1. The temperature dependence of the inverse paramagnetic susceptibility of TmCu$_2$. a,b,c indicate crystallographical axes, triangles represent experimental data [5] and full lines theoretical calculation. The corresponding fit parameters are included.

where E_n are the energies and $|n>$ the eigenvectors of the unperturbed Hamiltonian H_0, N is the dimension of the Hilbert space of the system and the relation $k(n+1) = k(1)$ is valid. The diagonal elements of the paramagnetic susceptibility tensor χ_i are then given by the formulae:

$$\chi_i = \chi_i^0 + \chi_i^c \quad ,$$ (13)

where

$$\chi_i^c = -\frac{d^2}{dh_i^2}\left(-\frac{1}{\beta}ln<\sigma>\right) =$$

$$= -\frac{1}{\beta}\left\{ \frac{1}{<\sigma>^2}\left(\frac{d<\sigma>}{dh_i}\right)^2 - \frac{1}{<\sigma>}\frac{d^2<\sigma>}{dh_i^2} \right\}$$ (14)

where χ_i^0 is the susceptibility of unperturbed system and χ_i^c is the correction given by the perturbation. It is obvious that for the further calculation one needs the explicit form of the dependence $\sigma(h_i)$. From (9) and (12) follows that to do this we have to express the dependences $E(h_i)$ and $|n(h_i)>$. This can be done by adding the Zeeman term $H_z = g\mu_B h_i J_i$ to the total Hamiltonian H and by using the standard quantum

mechanical perturbation theory. $E_n(h_i)$ and $|n(h_i)>$ are then given approximately:

$$E_n(h_i) = E_n + g\mu_B h_i < n|J_i|n> + g^2\mu_B^2 h_i^2 \sum_{m,m\neq n} \frac{|<n|J_i|m>|^2}{E_n - E_m}, \qquad (15)$$

$$|n(h_i)> = |n> + g\mu_B h_i \sum_{m,m\neq n} \frac{<m|J_i|n>}{E_n - E_m}|m> . \qquad (16)$$

The higher orders don't contribute to the calculation of the susceptibility in the limit of zero external field $h_i = 0$. Combining formulae (13),(14),(9) and (12) one can express the static susceptibility of the system in the form of a very large analytical expression, which we used in the numerical computations.

2. Application to $TmCu_2$

On the basis of the presented theory we have developed the numerical process for determination of parameters, which enter into the total Hamiltonian (3). The determination is based on the fitting of the calculated anisotropic paramagnetic susceptibility to the experimental data. We optimise simultaneously the crystal field parameters, anisotropic molecular field constants $\lambda_x, \lambda_y, \lambda_z$ and effective parameter I representing the additional influence of conduction electrons.

We have applied this numerical calculation to the $TmCu_2$ intermetallic compound studied in [5]. Our contemporary best fit to experimental data is shown in Fig.1.

By successive calculation of H_{CEF}, H_{mol} and H_{cond} contributions we have found that the influence of H_{cond} on the paramagnetic susceptibility of $TmCu_2$ is comparable with the effect of H_{mol}. The best fit we have obtained by simultaneous consideration of all the contributions to the total Hamiltonian (3).

References

[1] L.L. Hirst:: *Adv. Phys.* **27** (1978) 231

[2] S. Doniach, E.H. Sondheimer: *Green's Functions for Solid State Physicists.* The Benjamin Cummings Publishing Company, Reading 1974.

[3] V.G. Baryakhtar, V.I. Krivoruchko, D.A. Yablonsky: *Funkcii Grina v teorii magnetizma* AN USSR, Doneck 1985.

[4] Š.Zajac, F.Pešek: *IEEE Trans.Magn* **30** (1994) 899

[5] V.Šíma, M.Diviš, P.Svoboda, Z.Smetana, Š.Zajac, J.Bischof: *J.Phys.: Condens. Matter* **1** (1989) 1013