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A. A. Gomes, A. P. Guimarães and L. Iannarella

CENTRO BRASILEIRO DE PESQUISAS FÍSICAS

Av. Wenceslau Braz, 71 - Botafogo - ZC-82

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A. A. Gomes, A. P. Guimarães and L. Iannarella
Centro Brasileiro de Pesquisas Físicas
Rio de Janeiro, Brazil

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ABSTRACT

A simple s-, d-band model for the rare-earths is used to describe the g-shifts in metallic systems containing gadolinium. The temperature dependence of the d-electron susceptibility $\chi^{(d)}$ is suggested to explain the apparent discrepancies between the exchange parameters J_{eff} measured using different techniques (EPR, bulk magnetization measurements, hf fields). A numerical calculation shows that a model band with a narrow ($\sim$ 0.1 ev wide) peak near the Fermi level could account for the required variation of $\chi^{(d)}$ in gadolinium metal.

I. INTRODUCTION

Several authors have recently considered the Gd^{3+} g-shifts in intermetallic compounds and solid solutions containing gadolinium [1, 2]. The values of the exchange parameter J_{eff} derived from the g-shift measurements are in some cases in conflict with those obtained from other methods (see Maple [3]). It has been suggested by Coles and collaborators [4] that the negative g-shifts could be understood by assuming that the s- and d-electrons in the conduction band magnetize in opposite directions. The problem of s-d hybridization is discussed in another work [14].

2. BAND MAGNETIZATION AND g-SHIFTS IN THE RARE-EARTHS

We have taken into account the findings of band calculation in Gd [5] which show a transition-metal like band with a substantial d-electron density at the Fermi level. We start with a Hamiltonian for the interaction between the (s and d) conduction electrons and the localized spins $\vec{S}_n$, assumed of the usual form:

$$\mathcal{H}_n = - \sum_{i=s,d} J_{eff}^{(i)} \; \delta(\vec{r}-\vec{R}_n) \; \vec{S}_j \cdot \langle \vec{s}^{(i)}(\vec{r}) \rangle \qquad (1)$$

Following the conventional derivation [1] (in the limit of fast electron-lattice relaxation) the expression for the g-shift in such a metal is given by

$$\Delta g = \sum_{i=s,d} \frac{J_{eff}^{(i)} \chi^{(i)}}{g_e \mu_B^2} = \frac{1}{g_e \mu_B^2} \left\{ J_{eff}^{(d)} \chi^{(d)}(T) + J_{eff}^{(s)} \chi^{(s)} \right\} \qquad (2)$$

where

$$\chi^{(i)} = \chi^{(i)}(q=0) \ .$$

The d-part of the band susceptibility has been written $\chi^{(d)}(T)$ to emphasize the fact this is the part most dependent on the temperature. We are also assuming that the Van Vleck contribution χ^{VV} is small.

Besides g-shift measurements, other experimental techniques used to obtain the exchange parameters $J_{eff}^{(i)}$ include magnetization measurements and hyperfine field measurements. The net band magnetization at saturation is given within this s-, d-band model by:

$$m = \frac{1}{g_e \mu_B} \left\{ J_{eff}^{(d)} \ \chi^{(d)}(0) + J_{eff}^{(s)} \chi^{(s)} \right\} < S > \qquad (3)$$

The variation in the lanthanide hyperfine field in an intra-rare-earth solid solution is also dependent on the products $J_{eff}^{(i)} \chi^{(i)}$. The slope of the hf field versus average spin of the alloy can be shown to be [6]

$$\frac{dH}{d <\bar{S}>} = \frac{1}{g_e \mu_B} \left\{ - \alpha_{core}^{d} \ J_{eff}^{(d)} \chi^{(d)}(0) + A(Z) \ J_{eff}^{(s)} \chi^{(s)} \right\} \qquad (4)$$

where $\alpha_{core}^{d} \sim -$ 50 kOe is a core-polarization coefficient and A(Z) is related to the hyperfine constant [12]. The first term in (4) gives the core polarization hf field produced by the d-electrons in the band; the second term is the contact term with the band s-electrons.

If one applies expressions (2), (3) and (4) to a metallic system containing gadolinium, substituting reasonable estimate for $J_{eff}^{(i)} \ \chi^{(i)}$ one finds that the d- and s-electrons contributions differ markedly in importance

from one expression to the other. For instance, the band magnetization m (at $T = 0^{\circ}K$) is dominated by the d-electron term; on the other hand the slope in the graph of hyperfine fields versus concentration (in RE-RE alloys [6]) is almost entirely determined by the s-electron contact term.

From Eq. (2) we see that the g-shifts have contributions from both s and d susceptibilities; depending on the details of the band structure, the value of $\chi^{(d)}(T)$ at the experimental temperatures can be significantly different from $\chi^{(d)}(0)$ [13] (which appears in the magnetization) and more, a decrease of $\chi^{(d)}$ with temperature can possibly make the s-electron contribution to the g-shift dominant. This may result in a change in sign of the g-shift, since in many cases $J_{eff}^{(s)} < 0$ (although we always have $J_{eff}^{(d)} > 0$ [10]). We think that the variation of the d-susceptibility with temperature may explain some of the disagreements between measurements of J_{eff} using different techniques (which are performed at different temperatures).

Magnetization measurements in lanthanum and lutetium [11] show that the susceptibility decreases with temperature; it is likely that the d-band susceptibility in the magnetic rare-earth metals behave in the same way.

An example of a metallic system where the temperature dependence of the d-susceptibility could be important is gadolinium metal. The low temperature magnetization results [7] are consistent with a positive band magnetization (assuming a free-ion value for the Gd^{3+} moment) with $m \simeq 0.5\mu_B$; the g-shift at $T > 370^{\circ}K$ is negative, and $\Delta g \simeq -0.04$ [8, 9]. This can be understood if one has

$$|J_{eff}^{(d)} \chi^{(d)}(0)| > |J_{eff}^{(s)} \chi^{(s)}| > |J_{eff}^{(d)} \chi^{(d)}(T)|$$

and

$$J_{eff}^{(s)} < 0 .$$

The negative value of the s exchange parameter is normally associated to the large role of interband mixing [10], although this may not always be necessary [14].

Using expressions (2) and (3) for the g-shift Δg and the magnetization m, and the experimental values for these quantities, we obtain

$$J_{eff}^{(s)} \frac{\chi^{(s)}}{g_e \mu_B^2} \cong 0.14 - J_{eff}^{(d)} \frac{\chi^{(d)}(0)}{g_e \mu_B^2}$$

and

$$J_{eff}^{(s)} \frac{\chi^{(s)}}{g_e \mu_B^2} = - 0.04 - J_{eff}^{(d)} \frac{\chi^{(d)}(T)}{g_e \mu_B^2}$$

where $J_{eff}^{(d)} \chi^{(d)}(T)/g_e\mu_B^2$ is a positive quantity, since $J_{eff}^{(d)} > 0$. We therefore have

$$\frac{\chi^{(d)}(T)}{\chi^{(d)}(0)} = \frac{J_{eff}^{(d)} \chi^{(d)}(T)/g_e\mu_B^2}{0.18 + J_{eff}^{(d)} \chi^{(d)}(T)/g_e \mu_B^2} \qquad (5)$$

Taking a reasonable value of $J_{eff}^{(d)} \chi^{(d)}(T)/g_e\mu_B^2$, for instance 0.03 (which in turn leads to $J_{eff}^{(s)} \chi^{(s)}/g_e\mu_B^2 = - 0.07$), we have

$$\frac{\chi^{(d)}(T)}{\chi^{(d)}(0)} \cong \frac{1}{7}$$

The negative g-shift and the positive band magnetization could thus be comprehended if the high temperature d-band susceptibility was about seven

times smaller than its value at $T = 0^{\circ}K$. This is a very rough estimate since we expect the uncertainty in m to be of at least 20%; the spread in the values of Δg for Gd metal in the literature is of the same order of magnitude. From the hypothesis of $J^{(d)} \chi^{(d)}/g_e\mu_B^2 = 0.03$ and $\chi^{(d)}(0)/g_e\mu_B^2 = 1.5\ ev^{-1}$ (estimated from $N(\varepsilon_F) = 1.8\ ev^{-1}$ [5]) we derive $J^{(d)} \approx 0.14$ and $J^{(s)}_{eff} \approx -0.2$ for gadolinium.

3. A MODEL BAND FOR GADOLINIUM METAL

It is well known that if the Fermi level at $0^{\circ}K$ is near a maximum in the density of states, the band susceptibility decreases with increasing temperature. Starting from this basic idea we have attempted to devise a model for the band structure of gadolinium metal which could account for a drop in magnetic susceptibility to 1/5 - 1/10 of its saturation value.

The magnetic susceptibility is given by [13]

$$\chi = \frac{\mu_B}{H} \left\{ \int_0^{\infty} \frac{N(\varepsilon)d\varepsilon}{\exp((\varepsilon - \varepsilon_F - \mu_B H)/kT) + 1} - \int_0^{\infty} \frac{N(\varepsilon)d\varepsilon}{\exp((\varepsilon - \varepsilon_F + \mu_B H)/kT) + 1} \right\} \tag{6}$$

where the Fermi level ε_F has to be computed at each temperature. Since the above expression gives a non-zero contribution only in a region of width $\sim kT$ around the Fermi level, the dependence of the susceptibility with temperature is related only to the band structure within this narrow energy range. Numerical calculations using expression (6) were performed by assuming a peak in the density of states centred at $\varepsilon_F(T = 0^{\circ}K)$; the width

of this line (of lorentzian shape) was made to vary, keeping constant the height N = 1.8 ev^{-1} [5]. Since the g-shifts are usually determined by extrapolating (e.g. [18]) the measured shifts to $\frac{1}{T-\theta} = 0$ (to eliminate the contribution from the localized moments which follows a Curie-Weiss law) we have followed a parallel procedure: the susceptibilities were computed at different temperatures in the range 400-600 ^{o}K and then extrapolated to $T = \infty$.

This showed that we could, with a line 0.1 ev wide (full width at half maximum), produce a drop in the susceptibility to 1/5 of its low temperature value. This result is in rough accordance with the assumptions of section 2.

Another possibility which could alternatively explain the conflicts between magnetization and g-shifts results would involve d-band lattice relaxation times such that the d- susceptibility would not contribute to the g-shifts.

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