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The crystal-field interactions in $NpGa_2$

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Abstract. The zero-temperature value of the local Np ordered magnetic moment ($2.39\mu_B$) in the ferromagnet $NpGa_2$, its temperature-dependence and the value of T_c (55 K) have been very well reproduced within the crystalline-electric-field (CEF) approach in combination with spin-dependent interactions considering the $5f^4$ configuration of the Np^{3+} ion. The derived fine electronic structure of the $^5I_4$ multiplet, with the set of CEF parameters $B_2^0 = -9.4$ K, $B_4^0 = -45$ mK, $B_0^6 = +0.7$ mK and $B_6^6 = -14$ mK, has the non-Kramers doublet Γ_5 as the charge-formed ground state and the overall CEF splitting of 435 K. The good description provides strong evidence for the localized 5f magnetism of the neptunium ions in $NpGa_2$ and the trivalent state of the Np ion.

1. Introduction

Mössbauer studies have revealed a value of the Np local moment of $2.39\mu_B$, which can be easily understood assuming the Np^{3+} valence and a $^5I_4$ Hund's-rule ground state multiplet (Yaar *et al* 1992). The value of the magnetic moment has been inferred from the hyperfine field on the ^{237}Np nuclei that can be accurately measured by the Mössbauer effect. Its value has been found to be just that expected for the localized $5f^4$ system. This paper will exploit further this qualitative suggestion of Yaar *et al* (1992) about the good localization of the 5f electrons of the neptunium in $NpGa_2$.

The aim of the present paper is to gain more insight into the formation of the localized state of the f electrons of the Np ion. For this, we make use of the experience obtained in studies of the isostructural compound UGa_2, properties of which turn out to be well understood within the individualized-electron theory for rare-earth intermetallics that underlines the coexistence of a few electronic subsystems in an intermetallic compound and treats f electrons as largely localized (Radwański and Kim-Ngan 1995a, 1995b).

2. Theoretical outline

Hund's rule yields for the highly-correlated f^4 electronic system of the Np^{3+} ion the ground multiplet $^5I_4$ ($L = 6$, $S = 2$). The Russell–Saunders coupling scheme yields the total angular momentum $J = 4$, the Lande factor $g_L = \frac{3}{5}$, the paramagnetic effective moment $P_{eff} = 2.68\mu_B$ and the maximal ordered moment $m_0 = gJ\mu_B = 2.4\mu_B$. The lowest multiplet is $2J+1$ =ninefold degenerate with respect to J_z values. The hexagonal-symmetry CEF interactions remove this degeneracy, forming three doublets ($2\Gamma_5$ and Γ_6) and three singlets (Γ_1, Γ_3 and Γ_4) (Abragam and Bleaney 1970). Their energy separations and the shape of the eigenfunctions depend on the strength of CEF interactions. In fact, the energy

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scheme will have a lot in common with the scheme derived for the Pr^{3+} ion in hexagonal $PrNi_5$ (Kim-Ngan and Radwański 1995) because the Pr^{3+} ion and the Np^{3+} ion are systems described by $J = 4$.

The single-ion Hamiltonian of the $5f^4$ system of the Np^{3+} ion is considered in the form (Radwański and Kim-Ngan 1995a, 1995b, Radwański *et al* 1992)

$$H_R = \sum_{n=0}^{6} \sum_{m=0}^{n} B_n^m O_n^m(J, J_z) + \lambda g^2 \mu_B^2 (-J\langle J\rangle + \tfrac{1}{2}\langle J\rangle^2) \tag{1}$$

The first term is the CEF Hamiltonian written for the Hund's-rule ground state multiplet. The second term accounts for exchange interactions written in the molecular-field (MF) approximation with λ as the MF coefficient. For intermetallics, exchange interactions, or in general, spin-dependent (S-D) interactions, are most likely to result from an indirect exchange of the RKKY type mediated by the spin-polarization of conduction electrons, in which 5d or 6d electrons play an important role. These two terms refer to charge and spin interactions of the unfilled f shell with its surroundings.

The CEF Hamiltonian of hexagonal symmetry can be written as (Hutchings 1964)

$$H_{CEF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^6 O_6^6. \tag{2}$$

The Hamiltonian (1) allows calculations of the bound/localized states of the f^n system, namely their positions and eigenfunctions $|LSJJ_z\rangle$. Having the eigenfunctions one can calculate expectation values of $\langle J_z\rangle$ and $\langle J_x\rangle$ for each local state and subsequently the magnetic moment of each state. The energy separations determine the temperature-dependence of the specific heat and the susceptibility in the paramagnetic region. With increasing temperature the magnetic moment of the excited states comes to be important because they are becoming populated according to the Boltzmann factor. Because the reverse procedure is very troublesome it results in long-lasting and still endless discussions of experimental results for a number of compounds. In fact, there are only a few compounds for which a full set of CEF parameters has been derived. The biggest problem is, after acceptance of the physical adequacy of the CEF approach, the determination of CEF parameters. First, they are small numbers. In comparison to the conventional band width of about 1 eV even in the case of narrow-band systems, the overall CEF splitting is only a small part of this. For instance, in $NpGa_2$ the overall CEF splitting is 435 K ($\simeq$ 40 meV), which amounts to $\frac{1}{25}$ of such a narrow band. The next difficulty lies in the fact that the CEF approach is nonlinear. The value of the ground-state magnetic moment, for instance, is not a smooth function of CEF parameters, especially not in the case of the level crossing and changing of the CEF ground state. Because the CEF parameters are associated with the charge distribution around the paramagnetic ion it means that the ground-state properties are not a smooth function of the charge distribution. It violates the basic assumption of the density functional theory. For formation of the magnetic ordered state the second term is indispensible. It is obvious to remember that, by the formation of the magnetic state, the system gains the energy that is calculated in the second term.

3. Discussion and results

From the start, we have used the CEF parameters obtained from CEF parameters found for UGa_2 (Radwański and Kim-Ngan 1995a, 1995b). They have been re-scaled using the Stevens coefficients (Abragam and Bleaney 1970, Hutchings 1964) $\alpha = -0.643 \times 10^{-2}$, $\beta = -2.91 \times 10^{-4}$ and $\gamma = -38 \times 10^{-6}$ for the U^{3+} ion and $\alpha = 0.771 \times 10^{-2}$, $\beta = 4.08 \times 10^{-4}$ and $\gamma = 60.8 \times 10^{-6}$ for the Np^{3+} ion. Note that Hutchings (1964)

and Fulde and Loewenhaupt (1988) following Elliot and Stevens (1953) gave for γ(Np) a value 11 times bigger (668×10^{-6}), probably due to a misprint in the original paper of Elliot and Stevens (1953), where instead of 11^3 in the denominator a value of 11^2 has been printed. The value 11^3 is given in table 20 of Abragam and Bleaney (1970). To our great surprise such an obtained set of CEF parameters gives the state Γ_5 (composed of atomic-like functions $|J_z = \pm 4\rangle$ and $|J_z = \mp 2\rangle$) as the ground state, namely the state that can realize the maximal moment of the $^5I_4$ multiplet. Indeed, the found state exhibits a large magnetic moment (of $2.20\mu_B$), the fact that is highly desired in order to reproduce the experimentally derived moment. For the complete reproduction of the experimental value, the value of the parameter B_6^6 has been reduced by a factor of five (in absolute value) from -69.5 mK to -14 mK (figure 1). Thus in calculations the following CEF parameters have been used: $B_2^0 = -9.4$ K, $B_4^0 = -45$ K, $B_6^0 = +0.7$ mK and $B_6^6 = -14$ mK. This set of CEF parameters yields the energy level scheme with the non-Kramers doublet ground state Γ_5 being an almost pure $|\pm 4\rangle$ state and exciting levels at 240 (singlet), 310 (singlet), 421 (singlet), 425 (doublet) and 435 K (doublet), see figure 2. The ground-state eigenfunction is $|\Gamma_5\rangle = 0.998|\pm 4\rangle + 0.063|\mp 2\rangle$. The magnetic properties of the ground state are very anisotropic, as one can infer from the very different expectation values of $\langle J_i \rangle : \pm 3.98$ and 0, respectively. These values determine properties of the ground state like the magnetic moment $m_i = -g_L \langle J_i \rangle \mu_B$ and the spectroscopic g_i factors, $g_i^{sp} = 2g_L \langle J_i \rangle$.

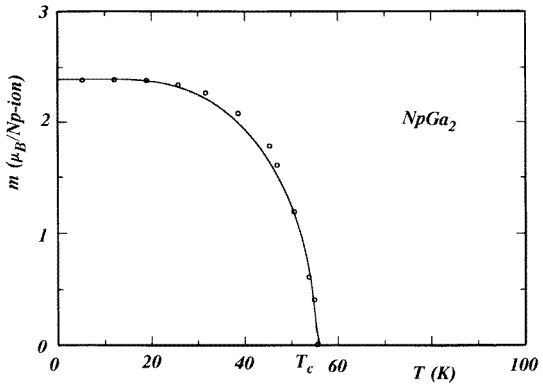

Figure 1. The temperature variation of the magnetic moment of the Np^{3+} ion in $NpGa_2$ calculated for the $5f^4$ localized system under the combined action of hexagonal CEF interactions ($B_2^0 = -9.4$ K, $B_4^0 = -45$ mK, $B_6^0 = +0.7$ mK, $B_6^6 = -14$ mK) and spin-dependent interactions approximated by the molecular-field coefficient $\lambda = 14.5$ T per formula unit/μ_B. Points are data measured by means of Mössbauer spectroscopy by Yaar *et al* (1992). It is worth noting that the calculated temperature-dependence is well approximated by the Brillouin function for $J = \frac{1}{2}$.

For $NpGa_2$ there exist no inelastic-neutron-scattering results that could provide the energetic positions of at least some of the states. The energetic positions are hidden within the temperature-dependences of different properties. From these we know the temperature-dependence of the Np hyperfine field. The hyperfine field is generally accepted to reflect the temperature-dependence of the local magnetic moment. The temperature-dependence of the susceptibility exists within a limited temperature range only (140–240 K). Moreover, it is rather uninformative; it has been measured for a polycrystalline sample and the anisotropy of the susceptibility governed by CEF interactions was not revealed.

The magnetic-ordering temperature is governed by the second term in Hamiltonian (1)

in which spin-dependent interactions are written with λ as the molecular-field coefficient. Its value is derived by self-consistent calculations of the free energy of the system in order to reproduce the value of T_c. The present calculations were performed in exactly the same manner as the calculations for $ErNi_5$ (Radwański *et al* 1992), $NdNi_5$ (Radwański *et al* 1994) and UGa_2 (Radwański and Kim-Ngan 1995a, 1995b). The MF coefficient $\lambda = 14.5$ T per formula unit/μ_B was found. λ fulfils the relation $\lambda \cdot \chi_{CEF}(T_c) = 1$, where $\chi_{CEF}(T)$ is the CEF-only susceptibility for $T = T_c$. The ordering appears for the highest-susceptibility direction; in this case the hexagonal z direction.

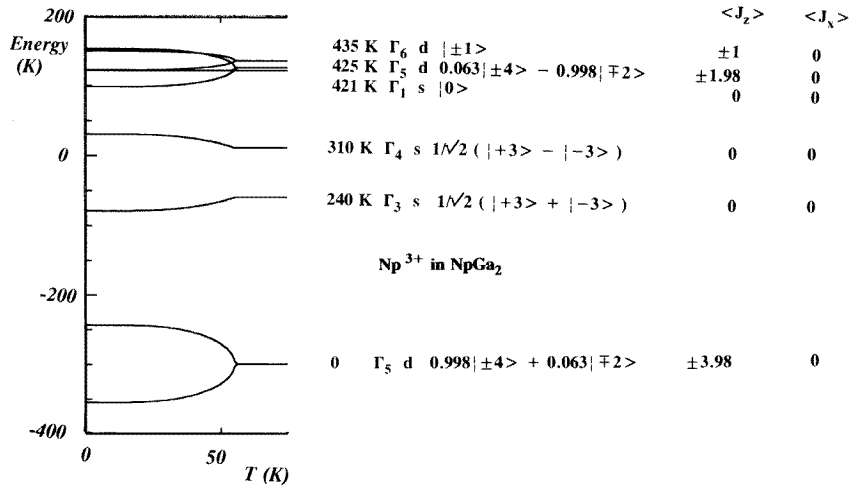

Figure 2. The energy-level scheme of the Np^{3+} ion ($5f^4$ configuration) in $NpGa_2$ and the appropriate eigenfunctions under the action of the hexagonal CEF interactions. The fine electronic structure contains three non-Kramers doublets and three singlets. The charge-formed ground state is a non-Kramers doublet Γ_5, the splitting of which is shown in figure 4. The exchange interactions split the CEF doublets below 55 K, forming the singlet magnetic ground state with the moment of $2.39\mu_B$ per Np ion at 4.2 K.

The most important results of the calculations are presented in figure 1. They are that (i) the magnetic moment of the Np^{3+} ion of $2.39\mu_B$ is in perfect agreement with the experimental value, (ii) the T_c value of 55 K is in perfect agreement with the experimental value, (iii) the temperature-dependence of the Np local magnetic moment is in very good agreement with that derived from the Mössbauer effect, (iv) the temperature-dependence of the f electron contribution c_f to the specific heat and (v) the temperature-dependence of the magnetic susceptibility in the paramagnetic region.

The temperature-dependence $c_f(T)$ cannot be verified at present because, to the best of my knowledge, it has not yet been measured for $NpGa_2$. However, for easier comparison, in figure 3 the total specific heat, including the lattice and band conduction-electron contributions, is shown. The lattice and conduction-electron contributions were calculated assuming them to be the same as those in the isostructural compound UGa_2 (the Debye temperature θ_D of 280 K and the Sommerfeld coefficient γ^c of 5 mJ K^{-2} mol^{-1}).

The magnetic state is associated with the appearance of the internal magnetic field and the removal of the double degeneracy of the Γ_5 ground state. The temperature-dependences of the two Γ_5 states are shown in figure 4. The temperature course of $c_f(T)$ is largely determined by the opening of this spin-like gap E_{sg} due to the fact that the excited CEF

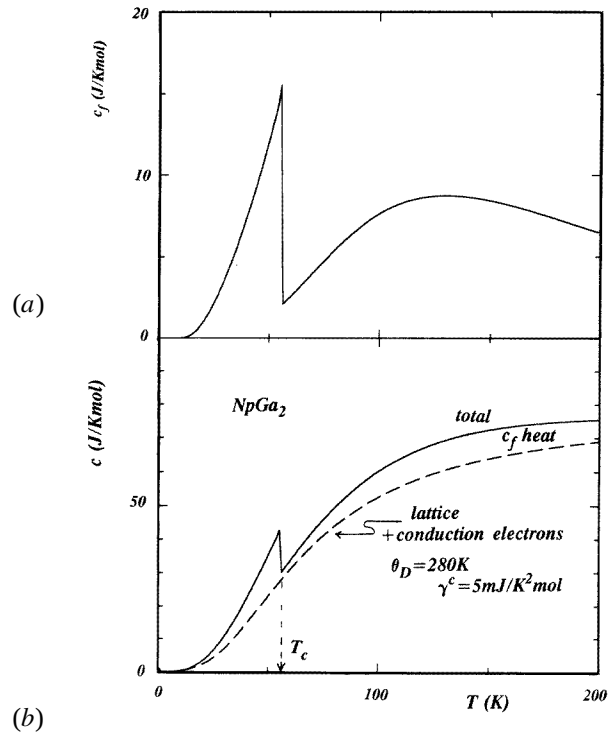

Figure 3. (*a*) The calculated temperature-dependence of the f contribution c_f to the specific heat of $NpGa_2$ (full line). (*b*) The total specific heat of $NpGa_2$. The broken line shows the electronic and phonon contribution evaluated with the Sommerfeld coefficient $\gamma^c = 5$ mJ K^{-2} mol^{-1} and the Debye temperature $\Theta_D = 280$ K (like in UGa_2). The contribution c_f due to the localized $5f^4$ systems is the difference between the full and the broken line.

states are relatively high. This spin gap opens at T_c and reaches a value of 110 K (= 10 meV) at 0 K. One should note that thermal excitations to the excited state are associated with the reversal of the local magnetic moment. Such a phenomenon has been observed for weak S-D interactions, as has been discussed by Radwański (1995). S-D interactions are regarded as weak when the S-D effect is much smaller than the separation between the ground state and the first excited CEF level. Thermally induced reversal of the magnetic moment within the well-separated doublet is a reason for the good description of the temperature-dependence of the magnetic moment by the Brillouin function for $J = \frac{1}{2}$ instead of $J = 4$. This is due to the fact that a well-separated doublet behaves as a pseudo-spin $S_{eff} = \frac{1}{2}$. We have checked it and found that the calculated temperature-dependence of the magnetic moment, shown in figure 1, is very well described by the Brillouin function for $J = \frac{1}{2}$. By the formation of the magnetic state the system gains the energy of 229 J mol^{-1} (= 27.5 K per formula unit) at absolute zero temperature.

4. Conclusions

The magnetic and electronic properties of $NpGa_2$ have been well described within the individualized-electron model assuming the coexistence of localized 5f electrons of the Np^{3+} ions and conduction elecrons, originating from the outer three electrons of Np and

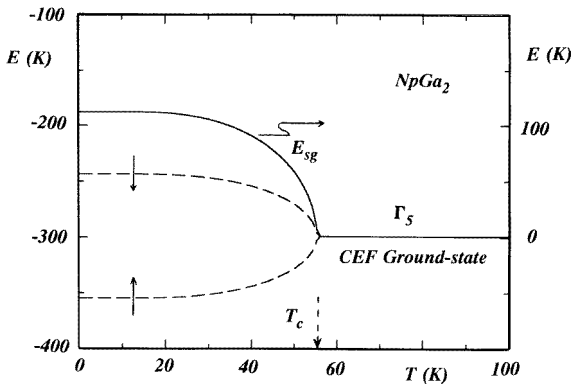

Figure 4. The splitting of the ground state Γ_5 of the f^4 non-Kramers system below T_c of 55 K (broken lines, left-hand scale). At T_c there opens the spin-like gap E_{sg} (full line, right-hand scale) that reaches at 0 K a value of 10 meV. This gap is caused by spin-dependent interactions of value $\lambda = 14.5$ T/μ_B. The internal field at 0 K amounts to 34.6 T. The temperature-dependence of the f electron specific heat, below 60 K, is largely determined by the opening of this gap because the other CEF levels are above 240 K. The arrows indicate the direction of the magnetic moment associated with each local state. The zero energy lies at the unsplit-multiplet level.

the outer electrons of Ga. The localized 5f electrons are largely responsible for magnetic properties and low-energy excitations, whereas conduction electrons are responsible for the metallic state and the Sommerfield coefficient γ^c. It is worth noting the obvious fact that the single-ion description of the f electrons does not contradict the collective nature of the magnetic state. The charge-formed (CEF) ground state of the $5f^4$ electrons is a non-Kramers doublet Γ_5 with the dominant $|J, J_z = \pm 4\rangle$ state. The description is really good in that the same set of CEF paramters and λ reproduces all basic magnetic and electronic characteristics of $NpGa_2$ and of the Np ground state, namely the spontaneous magnetic moment of $2.39\mu_B$, the value of the Curie temperature $T_c = 55$ K, the temperature-dependence of the magnetic moment and the paramagnetic susceptibility. This agreement is more remarkable owing to the fact that the found CEF parameters are related, by the single-ion formulae, to the parameters of UGa_2. These CEF calculations reveal the fine electronic structure (below 10 meV) associated with many-electron states of highly correlated f electron systems.

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