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The crystal field and exchange interactions in $NdNi_5$, UGa_2 and UPd_2Al_3

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Abstract

Magnetic and electronic properties of the hexagonal $NdNi_5$, UGa_2 and UPd_2Al_3 have been reviewed within a crystalline electric field approach in combination with exchange interactions. The fine electronic structure in these compounds associated with the Nd^{3+} and U^{3+} ions have been derived. The Nd^{3+} and U^{3+} ions, as Kramers f^3 systems, have the Kramers doublet ground state. In all compounds the Kramers doublet Γ_8 is the charge-formed ground state. The calculations reproduce all known experimental observations, in particular the observed ordered magnetic moment and Curie or Néel temperature.

Keywords: Actinides; f Magnetism; Crystal-field effects; Kramers degeneracy

1. Introduction

In conventional rare earth compounds, f electrons are found to be very well described within the localized-electron picture [1–3], whereas in unconventional rare earth compounds, such as Ce and Yb and mainly uranium, the f electrons seem to be highly delocalized [4–6]. Magnetic and electronic (ME) properties of the 4f intermetallic compounds have been well explained by the crystalline electric field (CEF) approach in combination with exchange interactions. There is also a growing number of uranium compounds which the ME properties can be understood within the CEF model [7–10], supporting the viewpoint of significant, if not full, localization of 5f electrons. The valency of the uranium in intermetallics, however, is still an open question, i.e. U^{3+} or U^{4+} ion, in contrast to ionic compounds such as UO_2 where the tetravalent state is rather expected.

In this paper experimental results of exemplary compounds $NdNi_5$, UGa_2 and UPd_2Al_3 are reviewed. All of them have hexagonal symmetry but quite different magnetic properties. It turns out that properties of UGa_2 and UPd_2Al_3 can be understood with the U^{3+} ions. The trivalent U ion has the f^3 configurations as the Nd^{3+} ion. Thus they have charge-formed (CF) Kramers doublet ground state. By joint analysis of ME properties the fine electronic structure associated with many-electron states of the Nd^{3+} as well as U^{3+} ions in these compounds is derived.

2. Experimental results for $NdNi_5$, UGa_2 and UPd_2Al_3: An overview

$NdNi_5$, UGa_2 and UPd_2Al_3 all crystallize in a hexagonal structure. $NdNi_5$, an intermetallic compound formed by rare earth metals with 3d transition metals, exhibits a ferromagnetic ordering below 7 K. The appearance of the magnetic order is indicated by a very pronounced λ type of peak in the specific heat [10]. The spontaneous moment at 1.5 K amounts to 2.1 μ_B f.u.$^{-1}$ (where f.u. denotes the formula unit of RNi_5) [2]. Most of this magnetization is associated with the Nd ions as Ni ions in the ordered state carry the magnetic moment of about 0.08 μ_B induced by the presence of magnetic Nd ions. High field single-crystal studies have revealed that magnetic properties are highly anisotropic with the easy magnetic direction along the *a* axis within the hexagonal plane [2,10]. The anisotropy is also present in the paramagnetic region [2].

UGa_2 orders ferromagnetically below $T_c = 125$ K [11,12]. Magnetic studies on a monocrystalline sample have revealed that the U moments are collinear along the *a* axis in the hexagonal plane [12]. The orthorhombic distortion, due to the spontaneous magnetostriction, is

observed in the ordered state [13]. The saturation moment reaches the value of 2.7 μ_B f.u.$^{-1}$. The paramagnetic susceptibility is largely anisotropic. A Curie–Weiss behaviour observed for the *a* axis yields the effective moment of 3.6 μ_B (U atom)$^{-1}$ [12].

UPd_2Al_3 exhibits antiferromagnetism below 14 K and superconductivity below 2 K [14,15]. It is also a heavy fermion system with a moderately enhanced specific heat coefficients γ at low temperatures of 150 mJ K^{-2} mol^{-1} [14,16]. Neutron diffraction studies have revealed long-range antiferromagnetic order with an ordered uranium moment of 0.85 μ_B coexisting with the superconducting state. Moments up to 1.70 μ_B have been found at external fields of 35 T [16]. UPd_2Al_3 is a unique system owing to the largest value of the uranium moment observed so far for any heavy fermion superconductor. The f electron specific heat of UPd_2Al_3 exhibits a λ type of peak at T_N and a well-pronounced Schottky type of peak centred at 55 K [15]. This specific heat has been attributed to excitations of the f electron subsystem over the localized states of the U^{3+} ions [17].

3. Fine electronic structure of the Nd^{3+} and U^{3+} ions

The Nd^{3+} ion and U^{3+} ion are $4f^3$ and $5f^3$ Kramers ions having three electrons. These ions, when placed in a solid, experience the electric field potential. As an effect of this potential the degeneracy of the partially filled f shell is lifted and different CF ground states of the f subsystem are realized. The lowest multiplet given by Hund's rules is $^4I_{9/2}$ with $J=9/2$, $S=3/2$, $L=6$ and the Landé factor $g=8/11$. The electric field produces the doubly degenerate Kramers doublet ground state. This double degeneracy, associated with the time-reversal symmetry, can be removed only by external or internal magnetic fields. The 10-fold $(2J+1)$ degenerate ground multiplet is split by the hexagonal CEF interactions of the form

$$H_{CF}=B_2^0O_2^0+B_4^0O_4^0+B_6^0O_6^0+B_6^6O_6^6 \quad (1)$$

into five Kramers doublets. The hexagonal term B_6^6 causes the mixing of the $|J_z\rangle$ states with J_z values different by ± 6. As a result, the atomic-like states $\pm 5/2$ are mixed with the states $\mp 7/2$ (Γ_8 states) whereas the states denoted by Γ_9 originate from the states $\pm 3/2$ mixed with the states $\mp 9/2$. The states $\pm 1/2$ denoted as Γ_7 are not affected by the term B_6^6.

The single-ion hamiltonian of the R^{3+} ion is considered in the form:

$$H_R=\sum_{n=0}^{6}\sum_{m=0}^{n}B_n^mO_n^m+\lambda g^2\mu_B^2[-J\langle J\rangle+(1/2)\langle J\rangle^2] \quad (2)$$

The first terms is the CEF hamiltonian and the second is exchange interactions written in the molecular field (MF) approximation with λ as the MF coefficient. For intermetallics, exchange interactions or, in general, spin-dependent (SD) interactions are probably an indirect exchange of the Ruderman–Kittel–Kasuya–Yoshida type mediated by the spin polarization of conduction electrons. The hamiltonian (2) allows for calculations of the bound-localized states of the f^n system, i.e. their positions and eigenfunctions. Having the eigenfunctions one can calculate expectation values $\langle J_z\rangle$ and $\langle J_x\rangle$ of each local state and subsequently the magnetic moment. The energy separations determine the temperature dependence of the specific heat and the susceptibility in the paramagnetic region. As the reverse procedure is very troublesome it results in long-lasting and still endless discussions of experimental results.

3.1. The Nd^{3+} ion in $NdNi_5$

The energy level scheme of the Nd^{3+} ion in $NdNi_5$ is presented in Fig. 1. All levels are doublets and they are split in the magnetic state. The CF ground state is Γ_8 and exhibits large anisotropy of magnetic characteristics as one can see from values listed in Table 1. As an effect of exchange interactions, $NdNi_5$ orders ferromagnetically at 7 K with the easy magnetic direction along the larger $\langle J_i\rangle$, i.e. the hexagonal *a* axis in this case. By the formation of the magnetic state the system of N neodymium ions gains magnetic energy: the magnetic singlet has at 0 K an energy lower by 7.9 K than the doubly degenerate CF ground state. The lifting of the double Kramers degeneracy is reflected in the large specific heat for $T<T_c$. The associated entropy amounts roughly to R ln 2 (R is the gas constant). Large specific heat at low temperatures is caused by many-electron

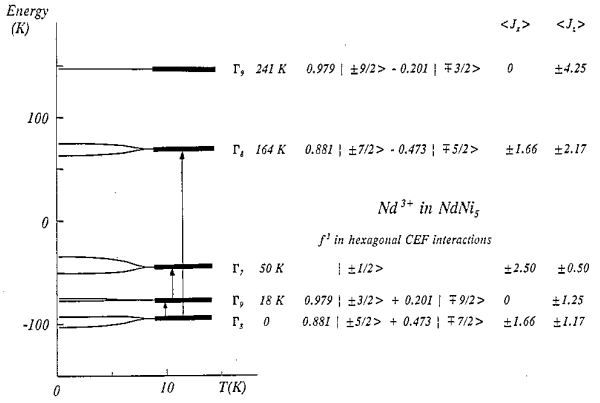

Fig. 1. The energy level scheme for the Nd^{3+} ion in $NdNi_5$ and the appropriate eigenfunctions and the expected values for $\langle J_z\rangle$ and $\langle J_x\rangle$ under the actions of CEF interactions of hexagonal symmetry. All levels are Kramers doublets. The exchange interactions split the CEF doublets below 7 K, forming the singlet magnetic state with a moment of 2.1 μ_B ion^{-1} at 1.5 K. The arrows indicate excitations seen in INS experiments.

Table 1
The characteristic parameters for $NdNi_5$, UGa_2 and UPd_2Al_3

	UGa_2	UPd_2Al_3	$NdNi_5$
Magnetic state	F	AF	F
T_c, T_N (K)	125	14	7.2
M (μ_B f.u.$^{-1}$)	2.7	0	2.1
m_{loc} (μ_B ion^{-1})	2.7	0.9–1.5	2.1
Configuration	U^{3+} (f^3)	U^{3+} (f^3)	Nd^{3+} (f^3)
B_2^0 (K)	+8.38	+7.5	+3.35
B_4 (mK)	+36.25	+60	+14.5
B_6^0 (mK)	−0.5	+0.07	−0.35
B_6^6 (mK)	−52	−32	−13.5
λ (T/μ_B)	40	−8.6	3.5
Δ_{CEF} (K)	713	629	241
CF ground state	Γ_8	Γ_8	Γ_8
I excited state	Γ_9 (102 K)	Γ_9 (105 K)	Γ_9 (18 K)
II excited state	Γ_7 (186 K)	Γ_7 (153 K)	Γ_7 (50 K)
III excited state	Γ_8 (557 K)	Γ_8 (338 K)	Γ_8 (164 K)
IV excited state	Γ_9 (713 K)	Γ_9 (629 K)	Γ_9 (241 K)
Internal field $B_{mol}^{U/Nd}$ (T)	108	14	7
$\langle J_x \rangle$ (ground state)	±1.88	±1.91	±1.66
$\langle J_z \rangle$ (ground state)	±0.51	±0.41	±1.17

excitations, over the shown bound states, which can be as small in energy as even a few kelvin. This f electronic specific heat contribution c_f is superimposed on single-electron excitations of conduction electrons. The CEF parameters listed in Table 1, resulting in the energy level scheme shown in Fig. 1, reproduce very well all known experimental facts such as values for the magnetic moment and T_c as well as the high field magnetization curves, the specific heat and inelastic neutron scattering (INS) experiments [2,10]. The INS experiments [18] yield excitations at 16.2 K, 33.6 K and 162.0 K (with an error estimated as ±2 K) whereas the present set gives 18.2 K, 32.2 K and 163.8 K respectively. The energy level scheme with the appearance of the splitting of the Kramers doublet in the ordered state is typical for Kramers systems. In the presence of SD interactions the CF ground state eigenfunction is substantially modified, which leads to the increase in the ground state magnetic moment. The SD interactions in $NdNi_5$ produce an effective molecular field B_{mol}^{Nd} of 7 T (Table 1) and an increase in the ground state moment from 1.21 μ_B to 2.1 μ_B.

It is worth noting that the ordered moment amounts to 2.1 μ_B. It is only 60% of the free ion value (3.27 μ_B). This reduction is fully understood as due to the CEF interactions. In Ref. [7] it has been shown that charge interactions can produce the ground state with largely reduced magnetic moment. This charge mechanism for the formation of the weakly magnetic state of a magnetic impurity is an alternative to the Kondo spin compensation mechanism [19].

3.2. The U^{3+} ion in UGa_2

There is strong similarity in magnetic and electronic properties of UGa_2 and $NdNi_5$ compounds such as the λ type of peak in the specific heat at the magnetic order temperature, the reduction in the magnetic moment due to CEF effect, and the high anisotropy of magnetic properties with easy magnetic direction along the a axis. The f^3 configuration of the U^{3+} ion reproduces well all properties of UGa_2. This means that uranium ions, if trivalent, have similar five Kramers doublet energy level schemes with the splitting appearing at a temperature dependent on the strength of SD interactions. Details of calculations will be presented elsewhere [20]. The energy level scheme for UGa_2 derived from the joint analysis of the electronic and magnetic properties of this compound is very similar to that presented in Fig. 1. The full set of CEF parameters is listed in Table 1. B_2^0 amounts to +8.38 K, two and half times bigger than that for $NdNi_5$, indicating stronger CEF interactions in uranium compounds. Although the second-order CEF term B_2^0 is the largest, it is higher-order CEF terms that make the doublet Γ_8 with the dominant ±5/2 states as the CF ground state. In the ordered state, all the doublets are split by exchange interactions, relevant at 4.2 K to an internal field of 108 T. The exchange interaction $\lambda = 40$ T/μ_B is about 10 times stronger than that of $NdNi_5$, owing to the larger extension of the 5f electron cloud. This set of parameters reproduces the ordered U moments m_U of 2.7 μ_B at 4.2 K and that it lies along the a axis as well as the value of T_c of 125 K. The good reproduction of the temperature variation of the specific heat, in particular, the λ type of peak at T_c, of m_U and the paramagnetic susceptibility (shown in Fig. 2), and the field dependence of magnetization along three principal

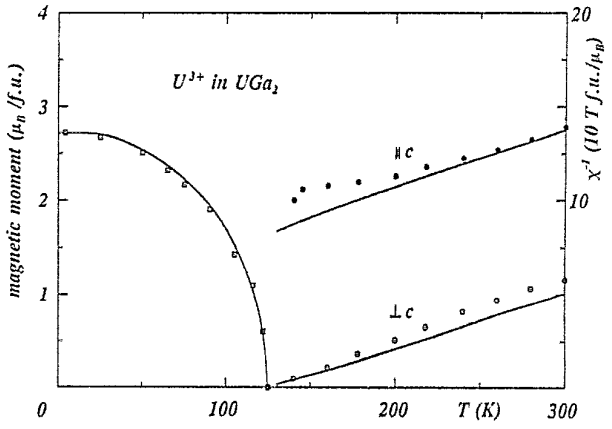

Fig. 2. The calculated temperature variation in the U^{3+} magnetic moment (left-hand scale) and of the reciprocal susceptibility (right-hand scale) resulting from the CEF parameters listed in Table 1. Points are data measured for the monocrystalline UGa_2, after Ref. [12].

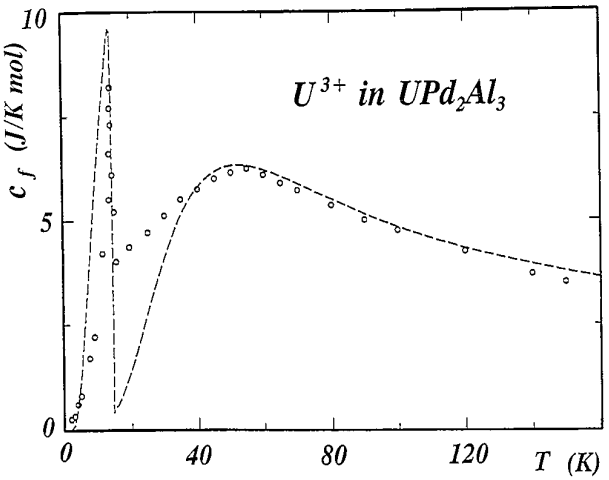

Fig. 3. Calculated temperature variation of the contribution of the U 5f subsystem to the specific heat of UPd_2Al_3 (– – –) resulting from CEF parameters listed in Table 1. Data are taken from Ref. [15].

axes of the hexagonal cell, provide strong support for the localized f electrons in UGa_2 and for the trivalent uranium valency in this compound.

3.3. The U^{3+} ion in UPd_2Al_3

The energy level scheme of the U^{3+} ions in UPd_2Al_3 has been derived from analysis of the specific heat for UPd_2Al_3 [16]. The set of CEF parameters is also listed in Table 1. These parameters for the f^3 configuration reproduce very well the overall behaviour of the magnetic specific heat, shown in Fig. 3, the λ type of peak at 14 K associated with the removal of the Kramers degeneracy, and the broad maximum located at 55 K, in particular. The position of the λ peak, marking the appearance of a long-range magnetic order, is determined by an MF coefficient λ of -8.6 T/μ_B, indicating that interactions in UPd_2Al_3 are about 3 times stronger than those of $NdNi_5$. The derived CF ground state Γ_8 is highly anisotropic with $\langle J_x \rangle = \pm 1.91$, $\langle J_z \rangle = \pm 0.41$. This large anisotropy is in agreement with single-crystal magnetic measurements [16]. In combination with exchange interactions a magnetic ground state with a moment of 1.72 μ_B (U ion)$^{-1}$ at 0 K along the *a* axis is formed. The U ion moment is strongly field dependent. For fields applied along the easy direction, it grows from 1.39 μ_B in the absence of fields to 1.95 μ_B at 30 T. For understanding of the magnetization curves, however, we have to take into account the antiferromagnetic interactions causing the zero resultant moment at zero field.

4. Conclusion

The electronic and magnetic properties of $NdNi_5$ are very well understood within the CEF model for f intermetallics in which f electrons are fully localized. The same model has been used for uranium intermetallics UGa_2 and UPd_2Al_3 and good agreement with experimental observations is obtained with the U^{3+} ions. All of these compounds have the CF ground state Γ_8 that results from higher-order charge multipolar interactions which are manifest in higher-order CEF terms. The anisotropic charge distribution in the vicinity of the f shell electrons causes a substantial reduction in the local magnetic moment. It is pointed out that the f electrons despite their good localization and the energetical position much below the Fermi level can provide in some f intermetallic compounds very substantial contribution to the specific heat at lowest temperatures. The present studies provide strong arguments for the substantial localization of 5f electrons and for trivalent uranium ions in UGa_2 and UPd_2Al_3. The latter conclusion seems to be quite important owing to the fact that most of CEF analyses for U compounds have been performed for the tetravalent state.

Acknowledgements

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