The anomalous temperature dependence of the f quadrupolar moment of the Nd^{3+} ion in $NdNi_5$

LETTER TO THE EDITOR

The anomalous temperature dependence of the f quadrupolar moment of the Nd³⁺ ion in NdNi₅

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Abstract. An anomalous temperature dependence of the quadrupolar moment of the Nd³⁺ ion in NdNi₅ has been calculated with the f electrons localized. The charge interaction can produce at low temperatures the localized state with quite a low value for the quadrupolar moment. These effects originate from higher-order crystalline-electric-field interactions. These studies prove that for the effective analysis of magnetic and electronic properties of the f intermetallics, all terms of the charge interactions have to be taken into account.

The quadrupolar moment can be measured by means of Mössbauer spectroscopy as an effect of interaction of the quadrupolar moment of the f shell with the nuclear quadrupolar moment. Within the f nuclei, most of the Mössbauer studies are on Yb compounds using the ^{174}Yb isotope [1,2]. The studies of Tomala *et al* [1] on YbCu₂Si₂ have revealed an anomalous temperature dependence of the Yb quadrupolar moment marked by (i) a maximum of the quadrupolar moment at $T \simeq 110$ K and (ii) quite a small value at $T = 4.2$ K. A theoretical explanation for this anomalous behaviour has been given by Zevin *et al* [3] in terms of the Anderson impurity model in which the crystalline-electric-field (CEF) interactions have been taken into account only by the first CEF term, i.e. the B_2^0 term. Another significant input *ansatz*, and later outcome, within this explanation is the variation of the number of f electrons with temperature.

The aim of this letter is to study the influence of higher-order CEF interactions on the f quadrupolar moment. In this letter the f^3 system like the Nd³⁺ ion in Nd Ni₅ is considered. NdNi₅ is an intermetallic compound, properties of which are well documented. It crystallizes in the hexagonal symmetry and exhibits ferromagnetic ordering below T_c of 7.2 K. For this compound the full CEF interactions of the hexagonal symmetry are known.

The quadrupolar moment of the f shell $Q_f(0)$ at $T = 0$ K is proportional to the expectation value of the second-order Stevens operator $\hat{O}_2^0$

$$\langle \hat{O}_2^0 \rangle = \langle 3\hat{J}_z^2 - \hat{J}^2 \rangle \tag{1}$$

where J and J_z are the total angular momentum of the incomplete f shell and its z component. This value is called the reduced quadrupolar moment $Q_f^r(0)$, where the superscript r indicates the reduced value. The proportionality factor contains, among others, the second-order Stevens factor α_J and the mean value of the radius of the f shell $\langle r_f^2 \rangle$. For the calculation of the temperature variation $Q_f^r(T)$ one has to make a thermodynamic average over the localized states, so
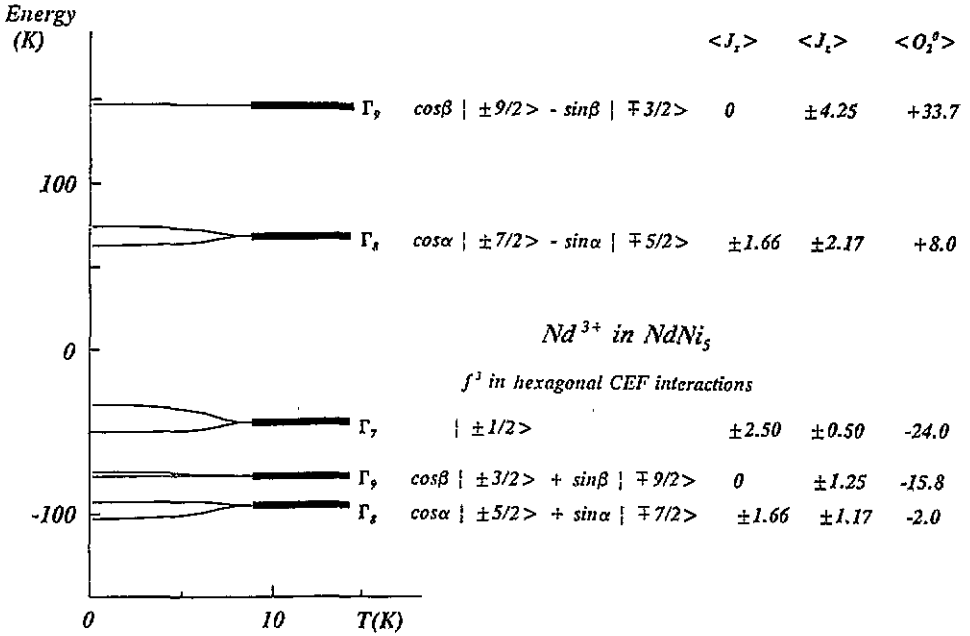
$$Q_f^r(T) = \langle 3J_z^2 - J(J+1) \rangle_T \tag{2}$$

$$\langle J_x \rangle \quad \langle J_z \rangle \quad \langle O_2^0 \rangle$$

Level	Eigenfunction	$\langle J_x \rangle$	$\langle J_z \rangle$	$\langle O_2^0 \rangle$
Γ_9	$\cos\beta \mid \pm 9/2 \rangle - \sin\beta \mid \mp 3/2 \rangle$	0	± 4.25	$+33.7$
Γ_8	$\cos\alpha \mid \pm 7/2 \rangle - \sin\alpha \mid \mp 5/2 \rangle$	± 1.66	± 2.17	$+8.0$
Γ_7	$\mid \pm 1/2 \rangle$	± 2.50	± 0.50	-24.0
Γ_9	$\cos\beta \mid \pm 3/2 \rangle + \sin\beta \mid \mp 9/2 \rangle$	0	± 1.25	-15.8
Γ_8	$\cos\alpha \mid \pm 5/2 \rangle + \sin\alpha \mid \mp 7/2 \rangle$	± 1.66	± 1.17	-2.0

Nd^{3+} in NdNi$_5$

f^3 in hexagonal CEF interactions

(Energy axis in K: 100, 0, -100; Temperature axis $T(K)$: 0, 10)

Figure 1. The energy level scheme for the Nd^{3+} ion in NdNi$_5$ under CEF interactions of hexagonal symmetry together with the eigenfunctions and the expected values for $\langle J_x \rangle$, $\langle J_z \rangle$ and for the reduced quadrupolar moment $\langle \hat{O}_2^0 \rangle$. All levels are Kramers doublets and they are split in the magnetically ordered state below T_c of 7.2 K where NdNi$_5$ becomes ferromagnetic. The CEF parameters are $B_2^0 = +3.35$ K, $B_4^0 = +14.5$ mK, $B_6^0 = -0.35$ mK, $B_6^6 = -13.5$ mK and the molecular-field coefficient between the Nd moments amounts to 3.5 T f.u./μ_B. $\cos\alpha = 0.881$ and $\cos\beta = 0.979$.

where $J(J+1)$ is the expectation value of $\hat{J}_2$.

The f^3 system within the LS scheme has $J = 9/2$ and the Hund's rules ground multiplet is $^4I_{9/2}$. Charge interactions of the hexagonal symmetry lift the tenfold degeneracy and produce five Kramers doublets. For the exemplary evaluation of $Q_f^r(T)$, the CEF parameters derived for NdNi$_5$ (Nd^{3+} is the f^3 system) have been taken: $B_2^0 = +3.35$ K, $B_4^0 = +14.5$ mK, $B_6^0 = -0.35$ mK and $B_6^6 = -13.5$ mK [4,5]. This set of CEF parameters describes consistently all known experimental results for NdNi$_5$, namely anisotropic magnetization curves measured on the single crystal up to 15 T [4], the temperature variation of the specific heat [5] and (localized) excitations observed in inelastic-neutron-scattering experiments [6]. The energy level scheme of the Nd^{3+} ion in NdNi$_5$ resulting from these charge interactions is shown in figure 1 together with the associated eigenfunctions and the expectation values for the components of the total angular momentum $\langle J_x \rangle$, $\langle J_z \rangle$ and the reduced quadrupolar moment $\langle \hat{O}_2^0 \rangle$, related to each localized state.

The variation of the reduced quadrupolar moment of the f shell $Q_f^r(T)$ with temperature is shown in figure 2. It has anomalous behaviour owing to its non-monotonic dependence. $Q_f^r(T)$ at $T = 0$ K is equal to the quadrupolar moment of the ground state and its amounts to -2.0 in the present case. This value is one order of magnitude smaller than that expected for the axial CEF with the term B_2^0 only. That is, the quadrupolar moment amounts to -24 for a positive value for B_2^0, as then the state $\mid \pm 1/2 \rangle$ becomes the ground state, or $+36$ for the $\mid \pm 9/2 \rangle$ ground state obtained for a negative value of B_2^0.
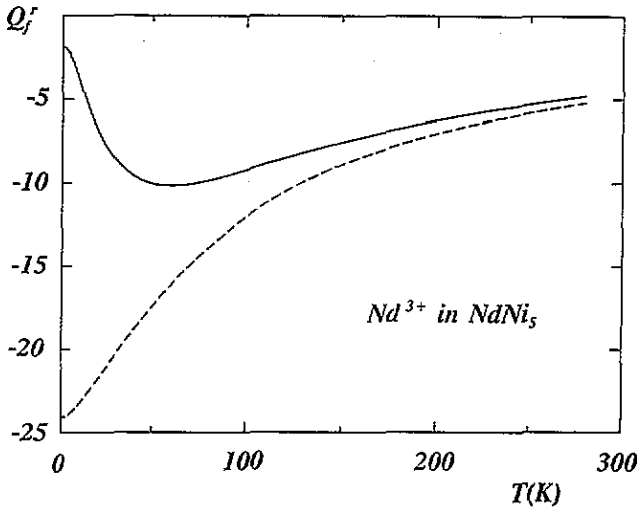
Figure 2. Temperature dependence of the reduced quadrupolar moment $Q_f^r(T)$ of the Nd^{3+} ion in $NdNi_5$ calculated within the CEF approximation with all terms of the CEF Hamiltonian of the hexagonal symmetry (solid line). For reasons of illustration the dependence of $Q_f^r(T)$ calculated with only the term B_2^0 of +3.35 K is also shown (broken line).

The anomalous temperature dependence can be explained as follows. In general, the non-monotonic behaviour results from higher-order CEF interactions. The B_2^0 term produces monotonic temperature behaviour, as shown by the broken curve in figure 2, as then the subsequent CEF levels have monotonically varied values for the quadrupolar moment -24, -18, -6, $+12$ and $+36$, respectively. Higher-order terms cause two effects: (i) the rearrangement of the CEF levels and (ii) the hybridization of the localized $|\pm J_z\rangle$ states produced by the term B_6^6. As a result, the ground state can have a smaller quadrupolar moment than the excited level. Indeed, the quadrupolar moment of the excited level is, in the absolute value, eight times larger than that of the ground state. As a consequence, thermal excitations to the first excited level cause a substantial increase (in the absolute value) of the quadrupolar moment of the f shell. This increase is limited by excitations to higher excited levels and quadrupolar moment tends to zero at temperatures comparable with the overall CEF splitting. Note that the sum of $Q_f^r(0)$ over all states is zero.

A direct comparison with experimental results is impossible, at least at present, because of the lack of evaluation of $Q_f^r(T)$ for the Nd^{3+}, Pr^{2+}, U^{3+} or Np^{4+} ions owing to scare experimental studies of these ions by Mössbauer spectroscopy. These results, however, could aid understanding of the anomalous temperature dependence of the quadrupolar moment of the ytterbium ions measured by Tomala *et al* [1].

In summary, the temperature dependence of the quadrupolar moment of the f shell has been calculated within the CEF approximation and anomalous, non-monotonic, dependence has been revealed. This non-monotonic dependence results from higher-order CEF interactions. These studies prove that, for the effective analysis of magnetic and electronic properties of f intermetallics, all terms of the charge interactions have to be taken into account.

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