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Crystal-field calculation of Pr^{3+} in orthorhombic PrNi_2Al_5 from ^{27}Al NMR Knight shift

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Abstract

The crystalline-electric-field (CEF) parameters for the Pr^{3+} ion in nonmagnetic PrNi_2Al_5 has been estimated using the ^{27}Al nuclear magnetic resonance (NMR) Knight shift, K , measured in a grain-aligned sample in the temperature range 3.5–310 K. The behaviour of the shift is well explained by van Vleck paramagnetism. The overall crystal-field splitting (Δ), obtained from the temperature dependence of K , is at least 100 K more than the value reported from magnetic susceptibility measurements. Moreover, the first two low lying excited states are 44 and 96 K above the ground level.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The relative strength of the crystalline electric-field effect (CEF) and the RKKY interaction generally determines the low temperature properties of rare-earth intermetallic compounds. The series of ternary intermetallics RENi_2Al_5 ($\text{RE} = \text{La}, \text{Ce}$ and Pr) is no exception. However, CeNi_2Al_5 is a dense Kondo compound ($T_K = 4$ K) with antiferromagnetic ordering $T_N = 2.6$ K [1], and the Kondo effect, along with consideration of the CEF, seems to be essential in the interpretation of the results [2]. PrNi_2Al_5 , on the other hand, is nonmagnetic down to 2 K [3]. The magnetic susceptibility, however, shows large anisotropy. To explain the susceptibility and the magnetic part of the specific heat C_{mag} , a CEF scheme has been proposed [3]. This shows that PrNi_2Al_5 has a singlet ground state with the energy level of the 4f electrons being split into nine singlets. The calculated result, however, shows a discrepancy (due to the presence of small impurities) in the reciprocal susceptibility below 10 K. To explain C_{mag} , only the three lowest energy levels were considered. Thus the CEF result using susceptibility reveals a total energy splitting width of 550 K, and the first and

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the second excited states are 19 and 54 K, respectively. However, from C_{mag} they are 43 and 80 K, respectively. Thus there is scope to check the CEF parameters in this low symmetry system with a more accurate estimation. It may be noted that in orthorhombic PrPtAl, the 4f levels of Pr^{3+} ions split similarly into nine singlets due to the CEF having 21 and 70 K as the first and second excited states, respectively. Thus a nonmagnetic ground state is expected. However, neutron diffraction measurement shows a clear ferromagnetic ordering below 5.8 K, yet the specific heat shows no remarkable peak at T_c and the magnetic entropy at T_c is small, indicating a comparable energy gap between the ground state and the excited state of the CEF and the exchange interaction between the 4f electrons [4].

CEF calculation requires two steps: (1) to establish a CEF level scheme which includes matrix elements of the transitions and (2) to search for the true CEF parameter set by taking into consideration all experiments such as magnetic susceptibility, specific heat etc which depend on the crystal field splitting of the RE ions. The first step, i.e. choosing a suitable CEF level scheme for Pr^{3+} in the orthorhombic field, seems to be correct [3]. For the second step, ideally, a neutron scattering experiment would be most suitable for a reliable calculation. Nevertheless, in some cases it can be estimated quite accurately using the nuclear magnetic resonance (NMR) Knight shift, which is generally not influenced by the presence of small impurities. In this paper we report the detailed calculation of CEF effects and use it to explain the ^{27}Al NMR results in a grain-aligned sample in the temperature range 3.5–310 K. The preliminary NMR results were presented in ICM2006 at Kyoto [5].

2. Experimental details

A single-phase aligned sample of PrNi_2Al_5 was prepared as mentioned in [2]. XRD patterns for an aligned sample and that of the random powder suggest that the majority of the grains in the aligned powder have their b axes parallel to each other. Though the directions of easy and hard magnetization are the c - and a -axes, respectively, the magnetic anisotropy between the c - and b -axes diminishes at temperatures above 100 K, and, in particular, around 300 K the magnetization along the b and c -axes is same [3], where alignment has been made. ^{27}Al NMR experiments were performed on a Bruker MSL 100 spectrometer with a 7.04 T superconducting magnet. In the case of oriented samples, the direction of the applied field was always kept parallel to the b -axis. In a system such as PrNi_2Al_5 the effective Hamiltonian for a ^{27}Al nucleus with spin $I = 5/2$ in the presence of a magnetic field H_0 is written as

$$H = H_0 + H_{\text{cond}} + H_M + H_Q, \quad (1)$$

where H_0 is the Zeeman term and H_{cond} represents the magnetic coupling between the conduction electron spin and the nuclear spin, and is temperature independent. The term H_M arises due to the interaction of the 4f electrons with the probed nuclei, via the conduction electrons, and is temperature dependent. H_Q is the quadrupole interaction. Assuming that the principal axes of the electric-field-gradient (EFG) tensor and the magnetic shift tensor are coincident, the experimental spectra have been fitted theoretically. The details can be seen, for example, in [6]. Figure 1 shows a typical frequency swept ^{27}Al spectrum of PrNi_2Al_5 along with the theoretically fitted line. Two pairs of clearly resolved satellite transitions consistent with the two nonequivalent Al sites were observed. Henceforth, we shall denote them as Al(1) and Al(2) with a multiplicity of eight and two, respectively. Moreover, a well resolved central transition indicates that the Knight shifts (K) for the two Al sites are completely different. Shift and the EFG parameters for two Al sites have been listed in [5].

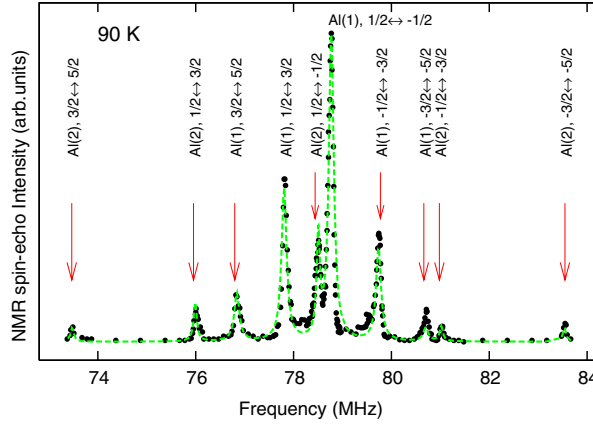


Figure 1. Typical ^{27}Al NMR spectrum of grain-aligned (b -axis) PrNi_2Al_5 at 7.04 T at 90 K. The continuous line indicates the theoretically fitted spectrum. The different transitions for Al(1) and Al(2) are marked by arrows.

3. ^{27}Al NMR Knight shift in PrNi_2Al_5

The Knight shift of a nonmagnetic rare-earth based intermetallic compound can be written as [7]

$$K(T) = K_0 + K_{\text{dip}}(T) + K_f(T), \quad (2)$$

where K_0 , a temperature independent term, has contributions mainly from the s contact term and d core-polarization terms and its magnitude can be estimated from similar shift measurement in a reference material, LaNi_2Al_5 [2]. K_{dip} is due to the electron-nuclear dipolar contribution to the total shift and can easily be calculated from knowledge of the lattice parameters and the temperature dependence of the magnetic susceptibility. The five independent components of the dipole-field tensor with respect to the crystallographic axes are determined from

$$H_d^{ij} = \sum \frac{3r^i r^j - r^2 \delta_{ij}}{r^5} \langle \mu \rangle, \quad i, j = x, y, z. \quad (3)$$

Here, $\langle \mu \rangle$ corresponds to the moment of the Pr^{3+} ion and is calculated from the relation $\langle \mu \rangle = \chi_M \mathbf{H} / N$, χ_M being the molar susceptibility determined for an oriented sample using a SQUID magnetometer (Quantum Design MPMS XL). It has been observed from the lattice summation calculation that, for each Al site, consideration of all of the neighbouring metal ions contained within a sphere of radius of 50 Å is sufficient for the calculation of H_d . For the Al(2) site, the diagonal components lie along the crystallographic axes and the off-diagonal components vanish, consequently $K_{\text{dip}} = (H_d / \mathbf{H})$ can be calculated along a suitable crystallographic direction. For Al(1), xy off-diagonal components do not vanish; thus we need to take, in addition to the appropriate diagonal component, the projection of the xy off-diagonal components along the particular axis. The estimated K_{dip} for both Al(1) and Al(2) sites are shown in figure 2. $K_f(T)$ along the b crystallographic direction is obtained by subtracting an appropriate K_{dip} from the total shift. Thus the temperature dependence of $K_f \equiv K(T) - K_0 - K_{\text{dip}}$ for two Al sites has also been plotted in figure 2. $K_f(T)$ arises due to s - f exchange interaction and is related to the transferred hyperfine field H_{hf} by

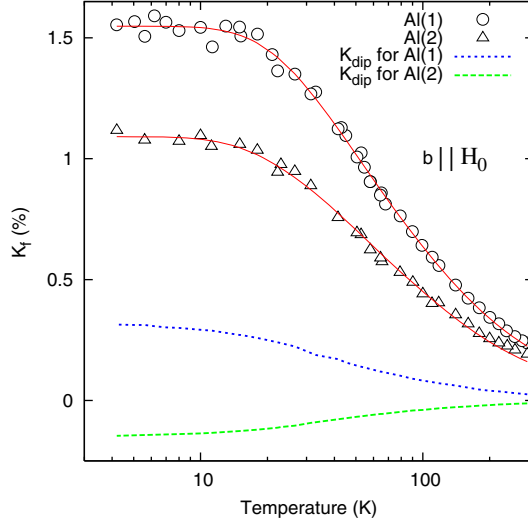


Figure 2. Temperature dependence of ^{27}Al Knight shifts for Al(1) and Al(2) sites of PrNi_2Al_5 (corrected for K_{dip} and K_0 as mentioned in the text). The estimated K_{dip} is also shown. The continuous lines represent least-square fit to equation (4).

$$K_f(T) = \frac{H_{\text{hf}}\chi_f(T)}{N\mu_B} \quad (4)$$

N is Avogadro's number and μ_B is the Bohr magneton. Hence, $K_f(T)$ gives a measurement of the temperature dependence of local susceptibility, $\chi_f(T)$. In the following subsection, we shall show calculation of $\chi_f(T)$ for a Pr^{3+} ion in an orthorhombic crystal field.

3.1. Magnetic susceptibility

In the van Vleck formalism the magnetic susceptibility of RE based compounds can be written as [8, 9]

$$\chi = \frac{N\mu_B^2}{kT Z} \sum_{n,i} \left[\sum_j |\langle \phi_{n,i} | \boldsymbol{\mu} | \phi_{n,j} \rangle|^2 - 2 \sum_{j,m \neq n} \frac{|\langle \phi_{n,i} | \boldsymbol{\mu} | \phi_{m,j} \rangle|^2}{E_n - E_m} kT \right] \exp\left(-\frac{E_n}{kT}\right), \quad (5)$$

where $Z = \sum_n d_n \exp(-\frac{E_n}{kT})$. Here, $\phi_{n,i}$ and $\phi_{n,j}$ are the d_n degenerate eigenfunctions with energy E_n in the absence of a magnetic field. The $\boldsymbol{\mu}$ is the magnetic moment operator $\boldsymbol{\mu} = g_J \mathbf{J}$. The first summation in the first set of large parentheses is over matrix elements diagonal in energy that normally produce Zeeman splitting in first-order perturbation theory. Usually this term produces the dominant temperature dependent contribution to the magnetic susceptibility. However, in the case of a low symmetry site, for an ion with an even number of open-shell electrons like Ho^{3+} and Pr^{3+} , these first-order terms reduce to zero. The second summation involves terms that arise in second-order perturbation theory. In principle, these second-order terms would contribute to the temperature independent susceptibility; however, in the case of Pr^{3+} , having a lower site symmetry with nearly low-lying energy levels, they can give rise to the temperature dependent susceptibility. In the case of PrNi_2Al_5 , using the eigenvalues and the eigenfunctions obtained as indicated in the following subsection, it can be shown explicitly that the first term in the large parentheses becomes zero and the temperature dependence of the magnetic susceptibility is completely governed by the second term.

3.2. Crystal field analysis

The total Hamiltonian of the $4f^n$ configuration in a crystalline environment is

$$H = H_{\text{FI}} + H_{\text{CF}}, \quad (6)$$

where H_{FI} is the free ion part and H_{CF} , the crystal-field term, is generally treated by perturbation theory. In the irreducible representation, $H_{\text{CF}} = \sum_{ikq} B_q^k C_q^k(i)$, where $C_q^k(i)$ is the q th component of a spherical tensor of rank k for the i th electron and B_q^k is the crystal field parameters [10]. H_{CF} lifts $(2J + 1)$ fold degeneracy according to the site symmetry of the rare earth ion in the crystal lattice. In general, the crystal-field split states are a linear combination of the $|\alpha, J, M_J\rangle$ states (α represents the other relevant quantum numbers) and the degree of mixing depends on the strength on the crystalline electric field. In the weak-field approximation, which applies well on the rare-earth elements, the total angular momentum J of the f^n configuration remains a good quantum number and the J multiplets remain well separated compared to the intramultiplet splitting. This is true in the case of Pr^{3+} , where one can neglect the inter-configuration coupling, i.e. the admixture of states for different J multiplets [11, 12]. In such a case the crystal-field states can be calculated based solely on the ground-state splitting, using the Stevens' operator equivalents method [13], which can be written as [10]

$$H_{\text{CF}} = \sum_{lm} A_l^m \langle r^k \rangle O_l^m, \quad (7)$$

where $A_l^m \langle r^k \rangle$ represent the crystal field parameters ($\langle r^k \rangle$ is a radial integral involving $4f$ radial wave functions) and O_l^m are the Stevens' equivalent operators, respectively. Henceforth, we will use A_l^m instead of $A_l^m \langle r^k \rangle$. One advantage of the operator equivalent method, based on the Wigner–Eckart theorem, is that the matrix elements of the operators O_l^m can be calculated conveniently in the eigenbasis of J_Z , since they contain only angular momentum operators. The equivalent operators and the numerical factors occurring in the Wigner–Eckart theorem are tabulated by Hutchings [14]. Also the conversion from one formalism to another (Stevens' equivalent operators and irreducible representation) is achieved using c_{lm} in $A_l^m = (x_J/c_{lm})B_q^k$ as tabulated by Kassman [15]. The factors x_J are the $\alpha_J, \beta_J, \gamma_J$ given in [14] for $J = 4$.

The crystal-field site symmetry of the rare-earth in a RENi_2Al_5 type orthorhombic structure is $Immm$ (D_{2h}). A crystal field with this symmetry is characterized by nine real parameters. A site with this symmetry will, in principle, fully split the Pr^{3+} ($J = 4$) ground term ($4f^2, {}^3\text{H}_4$) into nine singlets. So, in this compound the CEF equation can be expanded as

$$H_{\text{CF}} = A_2^0 O_2^0 + A_2^2 O_2^2 + A_4^0 O_4^0 + A_4^2 O_4^2 + A_4^4 O_4^4 + A_6^0 O_6^0 + A_6^2 O_6^2 + A_6^4 O_6^4 + A_6^6 O_6^6. \quad (8)$$

By diagonalizing the CEF Hamiltonian, i.e. equation (8), one can obtain consistent sets of eigenvalues and eigenvectors by which the explicit determination of magnetic susceptibility (equation (5)) is possible. Usually estimation of the CEF parameters is made by least-square fitting the experimental susceptibility data using equation (5), as was done by Akamaru *et al* [3] using irreducible tensor operator method. However, susceptibility data might contain an impurity which generally dominates its behaviour, particularly at low temperature. Relatively accurate CEF parameters may be obtained by fitting the local susceptibility χ_f derived from the experimental shift data using equation [3]. This has been done by varying ten parameters which includes nine CEF parameters A_l^m and the hyperfine field H_{hf} experienced by the Al(2) site. Trial CEF parameters have been taken after necessary conversion of the data given in [3]. H_{hf} has been taken from the K_f against χ_f graph. In figure 2 the line drawn through the experimental points for the Al(2) site is the result of the least-square fit. The results (nine real CEF parameters, energy eigenvalues and corresponding energy eigenfunctions) obtained

Table 1. CEF parameters B_q^k (in Kelvin) determined from the fit to the local susceptibility measured from ^{27}Al NMR shift in PrNi_2Al_5 .

B_0^2	B_2^2	B_0^4	B_2^4	B_4^4	B_0^6	B_2^6	B_4^6	B_6^6
694	-639	95	183	682	249	219	106	164

Table 2. Eigenvalues E_i and eigenstates of H_{CF} determined from the fit to the local susceptibility measured from the ^{27}Al NMR shift in PrNi_2Al_5 .

E_i (K)	$ -4\rangle$	$ -3\rangle$	$ -2\rangle$	$ -1\rangle$	$ 0\rangle$	$ 1\rangle$	$ 2\rangle$	$ 3\rangle$	$ 4\rangle$
0	0.512	0.0	-0.394	0.0	0.404	0.0	-0.394	0.0	0.512
44	0.0	0.499	0.0	-0.500	0.0	0.500	0.0	-0.499	0.0
96	-0.699	0.0	0.101	0.0	0.0	0.0	-0.101	0.0	0.699
219	-0.486	0.0	-0.395	0.0	0.461	0.0	-0.395	0.0	0.486
275	0.0	-0.706	0.0	0.024	0.0	0.024	0.0	-0.706	0.0
409	0.0	0.500	0.0	0.499	0.0	-0.499	0.0	-0.500	0.0
516	0.101	0.0	0.699	0.0	0.0	0.0	-0.699	0.0	0.101
605	-0.022	0.0	-0.433	0.0	-0.789	0.0	-0.433	0.0	-0.022
637	0.0	-0.024	0.0	-0.706	0.0	-0.706	0.0	-0.024	0.0

from the least-square fitting are listed in tables 1 and 2. Using these CEF parameters and the relevant K_{hf} for Al(1), a theoretical shift is obtained and shown also in figure 2. Thus it is established that temperature variation of ^{27}Al NMR shift is well explained by the van Vleck paramagnetism.

Finally we would like to mention that the results give an overall CEF splitting of $\Delta = 637$ K, which is at least 100 K larger than the value obtained from susceptibility results, and the energy gaps from the ground state to the first and second excited state are 44 and 96 K, respectively. These energy differences, i.e. the ground state to the first and second excited state, are very close to those obtained from C_{mag} and larger than the value obtained from the susceptibility result [3].

4. Summary

We have calculated relatively accurate crystalline electric field parameters for Pr^{3+} in orthorhombic PrNi_2Al_5 by fitting the local susceptibilities derived from ^{27}Al NMR shift data measured in a grain-aligned sample in the temperature range 3.5–310 K. The behaviour of the shift data is well explained by van Vleck paramagnetism. The spin lattice relaxation rate at low temperature is needed to know the excitation dynamics in the CEF energy gap which might throw more light on this singlet nonmagnetic PrNi_2Al_5 .

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