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Interpretation of the magnetic order, neutron diffraction and ^{111}Cd PAC studies of NdScGe

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Abstract. NdScGe is a ferromagnet with T_C = 194(2) K. The magnetic moments of the Nd substructure order along the tetragonal c-axis just below T_C and undergo a gradual canting away from the c-axis upon cooling, commencing at around 165 K. We used neutron powder diffraction to show that the Nd magnetic moments lie 70(3)^o off the c-axis at 4 K [1]. The apparent discrepancy between our neutron diffraction results and those obtained using PAC [2] (a canting angle of around 32^o just below T_C , increasing to 45^o at 25 K) can be reconciled by placing the principal axis of the electric field gradient tensor in the tetragonal basal plane, rather than along the c-axis, as assumed in the PAC analysis. The unusual temperature dependence of the ^{111}Cd PAC quadrupole frequency at the Sc site, which was interpreted in terms of a lattice softening occurring near the Curie temperature, is shown to be a consequence of the fact that one cannot determine the sign of the quadrupole frequency from a PAC experiment. Finally, we show that the Nd magnetic moments in the canted regime have a [110] basal component rather than [100].

Introduction

The RScSi and RScGe (R = light rare-earth) intermetallic compounds crystallize in the CeScSi-type tetragonal structure which is derived from the La_2Sb-type (tI12) structure (*I4/mmm* #139). The R atom occupies the *4e* site (point group *4mm*), Sc is in the *4c* site (*mmm*) and Ge/Si is in a second *4e* site (*4mm*). The magnetism of these phases exhibits a wide variety, ranging from strong ferromagnetism ($T_C \sim 350$ K) in GdScGe [3, 4] to antiferromagnetism below 26 K in CeScSi [5]. PrScGe exhibits multiple magnetic transitions [6].

The magnetic order of the Nd substructure in NdScGe was studied by ^{111}Cd Perturbed Angular Correlation (PAC) in which the NdScGe is doped with ^{111}In which subsequently decays to the probe ^{111}Cd by electron capture [2, 7]. All available evidence suggests that the ^{111}In occupies the Sc *4c* site (for example, our point-charge crystal-field calculations of the three available sites (Nd, Sc & Ge) indicate that only the Sc site has a non-zero quadrupole asymmetry parameter: η = 0.15 was measured by PAC [2]).

On the basis of the PAC magnetic hyperfine field and the quadrupole frequency NdScGe was reported to be ferromagnetic below 200 K and canted away from the tetragonal c-axis by 30(5)^o at 188 K, 35(5)^o at 181 K and increasing to 45(3)^o at 25 K. Magnetometry measurements yielded a Nd magnetic moment at 10 K of only 2.0 μ_B, 61% of the 'free-ion' value of 3.27 μ_B. Furthermore, the unusual temperature dependence of the PAC quadrupole frequency at the Sc site was interpreted in terms of a lattice softening occurring near the Curie temperature.

In a previous paper [1] we showed that NdScGe is ferromagnetic below T_C = 194(2) K with the Nd magnetic moments lying along the tetragonal c-axis just below T_C. A canting away from the c-axis upon cooling commences at around 165 K. At 4 K, the Nd magnetic moments lie 70(3)^o off the c-axis. Our determination of the magnetic structure of NdScGe was subsequently confirmed in [8]. In this paper we show that the seemingly different 'canting angles' (neutron *cf* PAC) of (0^o *cf* 32^o, the average of the 188 K and 181 K results) and (68^o *cf* 45^o as T → 0) are, in fact, mutually consistent when one takes into account the orientation of the principal axes of the electric field gradient (EFG) tensor at the Sc (^{111}Cd) site.

We also show that the unusual temperature dependence of the ^{111}Cd PAC quadrupole frequency, upon which the claim of a lattice softening was based, is due to the fact that one cannot determine the sign of the quadrupole frequency from a PAC experiment. We also demonstrate that the principal Z-axis of the EFG at the Sc site is in the tetragonal basal-plane and the Nd magnetic moments in the canted regime have a [110] basal component rather than [100], information that cannot be extracted from neutron diffraction on a powder sample due to the tetragonal symmetry [9].

Experimental methods

Details of the preparation of the NdScGe sample can be found in our previous paper [1]. Neutron powder diffraction measurements were carried out on the DUALSPEC C2 high-resolution diffractometer at the NRU reactor, Chalk River, Ontario. The neutron wavelength was 1.3285(1) Å and all patterns were refined using the FullProf/WinPlotr suite [10, 11]. At room temperature the lattice parameters of NdScGe are a = 4.313(1) and c = 15.821(2) Å, with the c parameter showing an increase upon cooling due to magnetoelastic effects.

Results

Our neutron diffraction refinements, reported in [1], indicated that at 4 K the Nd magnetic moment in NdScGe attains the 'free-ion' value of 3.19(8) μ_B and is canted away from the tetragonal c-axis by 70(3)^o. The subsequent paper by Manfrinetti et al. [8] gives a canting angle of 54(2)^o but this is an underestimate because their refined Nd moment is 3.53(4) μ_B which is actually 8% larger than the 'free-ion' value. In the ^{111}Cd PAC investigation of NdScGe, Mishra and Dhar [2] found an angle between the hyperfine field at the probe nucleus (reflecting the Nd magnetic order) and the c-axis of around 32(8)^o just below T_C, which increased to 45(3)^o upon cooling to 25 K.

In Fig. 1 we show the canting angle of the Nd moments relative to the c-axis as a function of temperature, as determined from our neutron diffraction refinements. Just below T_C, the Nd moments are aligned along the c-axis and a canting away from the c-axis sets in at T_{SR} ~ 165 K. The apparent discrepancy between the PAC angle of 32(8)^o and our neutron diffraction angle of 0^o above T_{SR} can be resolved by considering the fact that PAC cannot determine the sign of the electric quadrupole interaction. In deriving the PAC angle of β = 32^o, which is the angle between the hyperfine magnetic field at the Sc (^{111}Cd) site (assumed collinear with the Nd moment) and the Z-axis of the EFG, Mishra and Dhar [2] assumed that Z(EFG) is along the tetragonal c-axis. The ^{111}In dopant in NdScGe used for the PAC measurements resides in the Sc site which has the point symmetry *mmm* so the XYZ axes of the EFG are coincident with the crystal ABC axes but there is no *a priori* correspondence regarding the exact relationships.

To illustrate this point, we consider the second-order angular term which arises when projecting the hyperfine magnetic field (moment), whose direction in the EFG frame is given by the polar angles (β, α), onto the principal Z-axis frame of the EFG,

$$\frac{1}{2}\left(3\cos^2\beta - 1 + \eta\sin^2\beta\cos(2\alpha) \right). \tag{1}$$

This second-order term equals +(0.56 ± 0.21) for the PAC angle β = 32(8)^o [2] with Z(EFG) along the c-axis, taking into account the error in β and the fact that the azimuthal angle α was not specified above T_{SR}. However, if Z(EFG) lies in the basal plane, our neutron diffraction determination that the Nd moment (hence field) is along the c-axis above T_{SR} yields β = 90^o and a value of –(0.50 ± 0.02) for this angular term. Once again, we note that PAC is insensitive to the sign of the electric quadrupole interaction in these experiments.

At low temperatures i.e. well below T_{SR}, the PAC angles (at 25 K) are $\alpha \sim 45^o$ and $\beta = 45(3)^o$ [2] whereas our neutron diffraction measurements show that the Nd moments are canted away from the crystal c-axis by $70(3)^o$ at 4 K. Taking the Z(EFG) along the c-axis, as in the PAC analysis [2], these angles yield a value of +(0.25 ± 0.08) for the second-order term in Eq. 1. However, if Z(EFG) lies in the basal plane as we suggest, our neutron diffraction determination that the Nd moment is canted by $70(3)^o$ from the c-axis at 4 K yields a number of possible values for the angular term, depending on the exact orientation of the three EFG axes and also on the orientation of the basal component of the Nd magnetic moment (either along [100] or [110]), as shown in Table 1. The best fit to the experimental value of +(0.25 ± 0.08) is +(0.19 ± 0.03) which corresponds to Z(EFG) in the basal plane, Y(EFG) lying along the tetragonal c-axis and the Nd magnetic moment canted towards the [110] direction. This latter piece of information cannot be determined by neutron powder diffraction on a tetragonal phase [9].

Table 1. Values of the angular term (Eq. 1) as a function of the orientations of the Nd moment and the XYZ axes of the EFG.

Nd moment basal projection	EFG axes *cf* crystal abc	Angular term (Eq. 1)
[100] $\phi = 0^o$	ZYX	+0.83
[100] $\phi = 0^o$	ZXY	+0.81
[100] $\phi = 0^o$	XZY	−0.44
[100] $\phi = 0^o$	YZX	−0.56
[110] $\phi = 45^o$	ZYX / YZX	+0.14
[110] $\phi = 45^o$	XZY / ZXY	+0.19

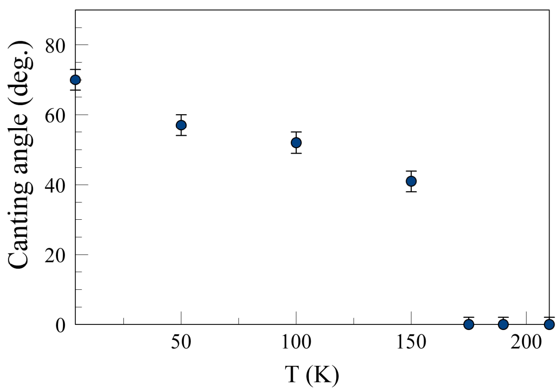

Figure 1. Temperature dependence of the canting angle of the Nd magnetic moments in NdScGe

Finally, we wish to address the question of a lattice softening which was claimed to occur around T_C, on the basis of the PAC work. The measured temperature dependence of the quadrupole frequency showed a pronounced dip around T_C which was ascribed to lattice softening. First of all, the magnetic hyperfine field just below T_C is quite small, making the determination of the hyperfine parameters somewhat unreliable. Secondly, PAC cannot 'see' the sign of the quadrupole interaction and we suggest that the different sign of the angular term discussed above serves to 'flip' the half of the temperature dependence of the quadrupole interaction term measured in the magnetic regime. PAC measures the magnitude of the quadrupole interaction, resulting in the pronounced dip reported in [2]. In Fig. 2 we show a schematic illustration of this effect.

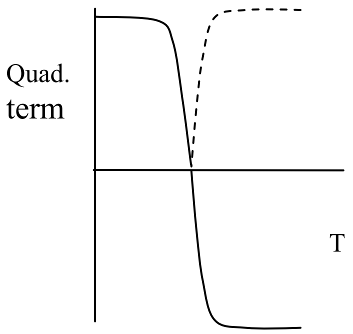

Figure 2. Schematic temperature dependence of the electric quadrupole term in the nuclear Hamiltonian at the Sc (^{111}Cd) site in NdScGe.

Summary

The Nd magnetic moments in the ferromagnet NdScGe order along the tetragonal c-axis at 194(2) K. At around 165 K, these moments cant away from the c-axis towards the [110] basal plane and at 4 K they lie 70(3)^{o} off the c-axis. The apparent discrepancies between our neutron diffraction results and previously reported PAC results regarding the orientation of the Nd moments can be reconciled by placing the principal axis of the electric field gradient tensor in the tetragonal basal plane, rather than along the c-axis, as assumed in the PAC analysis.

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