# Free-energy analysis of the single-$q$ and double-$q$ magnetic structures of neodymium

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A phenomenological model free energy is used to interpret the magnetic phase diagram of dhcp neodymium derived from recent neutron diffraction and thermal expansion measurements. First-order transitions at $T_N=19.9$ K and at $T_2=19.1$ K are to multidomain single-$q$ and double-$q$ modulated structures, respectively. The observed magnetic field dependence of these phases is in accord with the predictions of the model.

A succession of neutron diffraction studies[1] of the lanthanide element neodymium has revealed a rich variety of magnetically ordered phases below the Néel temperature, $T_N=19.9$K. However, a detailed understanding of the magnetic structures exhibited in these phases and of their magnetic field dependence has proved to be rather elusive. In this article, we present a phenomenological model free energy which allows us to comprehend many aspects of the magnetic phases of Nd.

As originally discovered by Moon *et al.*,[2] the neutron diffraction pattern immediately below $T_N$ is characterized by a hexagonal array of magnetic satellite reflections at wave vectors $\pm\mathbf{q}_1$, $\pm\mathbf{q}_2$, and $\pm\mathbf{q}_3$ along the three equivalent $b$ directions ($\langle 100\rangle$ in reciprocal space) around a general reciprocal point of the dhcp lattice [see Fig. 1(a)]. Alternative interpretations in terms of a multidomain single-$q$ state or a single-domain triple-$q$ state were first considered by Bak and Lebech.[3] Their renormalization-group analysis indicated that if the Néel phase transition were second order, the magnetic structure would be triple $q$, rather than single $q$. The available experimental evidence was consistent with a continuous transition and the triple-$q$ model was adopted.

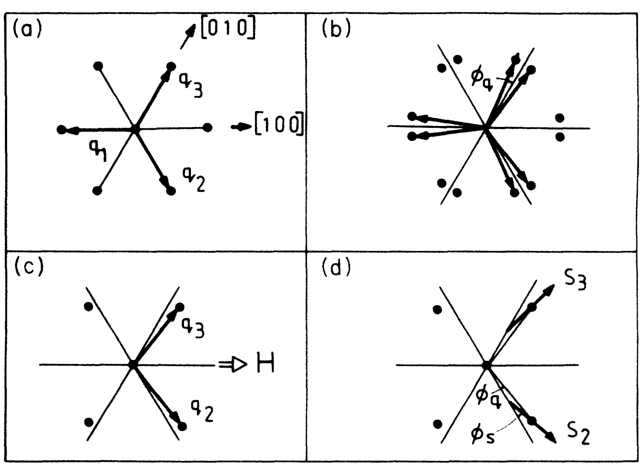


FIG. 1. Magnetic satellites observed around $(hkl)$: (a) for $T_2<T<T_N$; (b) for 8.3 K$<T<T_2$; (c) at $T=14$ K, with a magnetic field of 0.6 T applied in the direction indicated; (d) for a single domain of the double-$q$ structure, with moment directions shown.

In subsequent neutron diffraction work,[4,5] the satellite peaks were observed to split transversely, corresponding to a rotation of the modulation wave vectors $\mathbf{q}_i$ away from $\langle 100\rangle$ but within the basal plane [see Fig. 1(b)]. This rotation reaches a maximum of $\phi_q\sim 3°$ at around 14 K.[6] While the neutron data[1,6] suggest the existence of a second-phase transition at $T_2\simeq 19.3$ K below which the $\mathbf{q}_i$ rotate, heat-capacity measurements have, so far, failed to reveal this transition.[7] In this connection, Forgan[8] proposed a multidomain double-$q$ structure in which the rotation of $\mathbf{q}_i$ begins at $T_N$.

Recently, the nature of the Néel transition in Nd was reexamined in high-resolution thermal expansion measurements. The results of Zochowski and McEwen[9] are particularly significant as they reveal that (i) the Néel transition is actually first order and (ii) there exists indeed a *second* first-order transition at a temperature $T_2=19.1$K. Furthermore, the magnetic field dependence (for $\mathbf{H}$ along [100]) of $T_N$ and $T_2$ was also determined, as shown in Fig. 2. Additional phase transitions were measured, on heating the sample from a base temperature of 4.2 K, at 5.8, 6.3, 7.7, and 8.3 K, but we will not consider these phases in this article. The phases above 8.3 K (see Fig. 2) may be identified by reference to a neutron diffraction study of the magnetic field dependence of the satellite peaks at 14 K.[10] In these experiments, a field of 0.6 T applied parallel to [100] resulted in the disappearance of 8 of the 12 satellites of Fig. 1(b), leaving the pattern of Fig. 1(c), ascribed to a single-domain double-$q$ state. Just above the critical field $H_{c2}(T)$ of Fig. 2, the angle $\phi_q$ was found to be zero and at higher fields, slight variations of the field direction produced a strong asymmetry of the satellite intensities. From these results, it was concluded[10] that the zero-field state at 14 K is a multidomain double-$q$ state, and that there are two single-$q$ domains above $H_{c2}$.

We now interpret these results in terms of a model free energy. The spin density averaged over a unit cell is written

 

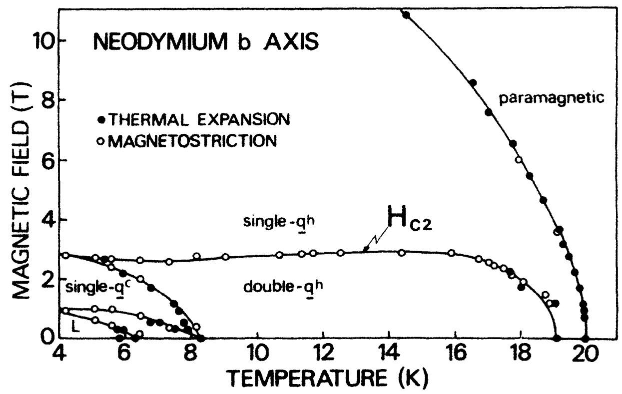


FIG. 2. Magnetic phase diagram of Nd deduced from thermal expansion and magnetostriction studies, after Ref. 9.

$$\mathbf{S}(\mathbf{r})=\sum_{i=1}^{n}\mathbf{S}_i\cos(\mathbf{q}_i\cdot\mathbf{r}+\phi_i)\ , \tag{1}$$

representing an $n$-tple q structure. The following free energy contains all terms, up to fourth order in $\mathbf{S}_i$, which are invariant with respect to a sixfold rotation about the hexagonal axis and with respect to time reversal:

$$F=\sum_i a(\mathbf{q}_i)S_i^2+a_1\sum_i(\mathbf{q}_i\cdot\mathbf{S}_i)^2 +u\left[\sum_i S_i^2\right]^2+w_1\sum_{i>j}S_i^2S_j^2+w_2\sum_{i>j}(\mathbf{S}_i\cdot\mathbf{S}_j)^2\ . \tag{2}$$

The first and second terms have their origins in the isotropic and anisotropic contributions to the exchange interaction, respectively. We assume that $a(\mathbf{q}_i)$ has its minimum value ($a_0$) for $\mathbf{q}_i$ along a $\langle 100\rangle$ direction and that $a_1<0$. Thus immediately below $T_N$, both $\mathbf{q}_i$ and $\mathbf{S}_i$ will be parallel to a $\langle 100\rangle$ direction, in agreement with observations.[1,6] In this case,

$$F=r\sum_i S_i^2+u\left[\sum_i S_i^2\right]^2+\left[w_1+\frac{w_2}{4}\right]\sum_{i>j}S_i^2S_j^2\ ,$$

where $r=(a_0+a_1q^2)$. From this expression, it is clear that if $w_1+w_2/4=w>0$, the free energy is minimized by the single-$q$ state ($S_1\neq 0$, $S_2=S_3=0$). If $w<0$, however, the triple-$q$ state with $S_1=S_2=S_3$ has a lower energy than either the single-$q$ state or a double-$q$ state (given by $S_1=0$, $S_2=S_3\neq 0$).

The region labeled single-$q$ in the phase diagram of Fig. 2 has been unambiguously identified as such by the neutron scattering experiments[10] in a magnetic field; moreover, the thermal expansion results[9] show no phase transition within this region, indicating that the single-$q$ phase extends to the interval $T_2<T<T_N$ in zero magnetic field. Thus we choose $w>0$ to stabilize the single-$q$ state. A first-order transition to a single-$q$ state at $T_N$ is consistent with the results of the renormalization-group analysis,[3] but a first-order transition to a triple-$q$ state would also be possible. As a final point, we note that for $w_2>0$ and $w>0$, no relative orientation of $\mathbf{S}_1$, $\mathbf{S}_2$, and $\mathbf{S}_3$ will yield a free energy [Eq. (2)] of the triple-$q$ state which is lower than that of the single-$q$ state; therefore the triple-$q$ state will be excluded from further consideration.

As the temperature is lowered further below $T_N$, the fourth-order terms in the $\mathbf{S}_i$ in Eq. (2) become relatively more significant than the second-order terms. Detailed analysis shows (and one could perhaps guess this result by looking at Eq. (2)] that provided $w_1<0$ ($w>0$ is still required) and at sufficiently low temperatures, the double-$q$ state with $\mathbf{S}_1=\mathbf{0}$ but $\mathbf{S}_2$ and $\mathbf{S}_3\neq\mathbf{0}$ [as shown in Fig. 1(d) for $\mathbf{H}=\mathbf{0}$] has a lower energy than the single-$q$ state. The model can thus account for a first-order single-$q$ to double-$q$ transition at some temperature $T_2<T_N$. At $T_2$, $\phi_s$ jumps discontinuously to a nonzero value and increases with decreasing temperature. Our analysis shows that $\phi_s(T)$, if extrapolated to temperatures $T>T_2$, tends to zero at $T_N$. The coupling term $(\mathbf{q}_i\cdot\mathbf{S}_i)^2$ in the free energy causes $\mathbf{q}_i$ to be tilted away from the relevant $\langle 100\rangle$ direction by the angle $\phi_q\propto\sin(2\phi_s)$.[11] Thus $\phi_q(T)$ is qualitatively similar to $\phi_s(T)$. This explains the "splitting" of the satellites below $T_2$ and the fact that the measured $\phi_q(T)$, if extrapolated to $T>T_2$, goes to zero at $T=T_N$. The 12-fold array of satellites shown in Fig. 1(b) results from the three coexisting double-$q$ domains.

The phase diagram for Nd in a magnetic field may be understood by adding to the free energy the contributions (up to fourth order):

$$F_H=-\mathbf{m}\cdot\mathbf{H}+\tfrac{1}{2}bm^2+\tfrac{1}{4}dm^4 +c_1m^2\sum_i S_i^2+c_2\sum_i(\mathbf{m}\cdot\mathbf{S}_i)^2\ , \tag{3}$$

where $\mathbf{m}$ is the homogeneous magnetization induced by the external magnetic field $\mathbf{H}$.

Since $c_2$ is positive, as will be shown below, $\mathbf{S}_i$ tends to become perpendicular to an applied magnetic field, like the staggered magnetization of a simple antiferromagnet. Hence, if $\mathbf{H}$ is applied parallel to the [100] direction, the double-$q$ domain with $\mathbf{S}_2$ and $\mathbf{S}_3$ nonzero is stabilized at the expense of the two other double-$q$ domains since each of the latter has a spin component almost parallel to the field [see Fig. 1(d)].

It was noted above that in the relatively low magnetic field of 0.6 T parallel to [100] the satellite pattern of Fig. 1(c) is produced (corresponding also to the spin directions of Fig. 1(d)]. The fact that $\phi_s$ and $\phi_q$ as defined in these figures are positive is reliable evidence that the observed satellite pattern represents diffraction from a single-domain double-$q$ structure. If the satellites at $\mathbf{q}_2$ and $\mathbf{q}_3$ represented diffraction from two single-$q$ domains, then $\phi_s$ and $\phi_q$ would be negative since the $c_2(\mathbf{m}\cdot\mathbf{S}_i)^2$ terms in $F_H$ forces $\mathbf{S}_i$ away from a $\langle 100\rangle$ direction to a direction where $\mathbf{S}_i$ is more nearly perpendicular to $\mathbf{H}$. In the double-$q$ structure, however, the interaction energy $w_2(\mathbf{S}_2\cdot\mathbf{S}_3)^2$ in Eq. (2) is minimized when $\mathbf{S}_2$ and $\mathbf{S}_3$ are perpendicular, and it is thus this term which produces the positive $\phi_s$ characteristic of the double-$q$ state.

As the magnetic field is increased in magnitude along a $\langle 100\rangle$ direction in the double-$q$ state the $(\mathbf{m}\cdot\mathbf{S}_i)^2$ terms in the free energy become more important than the $(\mathbf{S}_2\cdot\mathbf{S}_3)^2$ terms. Thus $\mathbf{S}_2$ and $\mathbf{S}_3$ are driven towards orientations more nearly perpendicular to the magnetic field and the

$(\mathbf{S}_2 \cdot \mathbf{S}_3)^2$ contribution increases and ultimately destabilizes the double-$q$ state relative to the single-$q$ state. Our analysis shows that at the double-$q$ to single-$q$ phase transition, the angle $\phi_s$ [as defined in Fig. 1(d)] changes discontinuously from a positive value to a negative value. The positive $\phi_q$ at low fields and its decrease with increasing field have been observed,[10] but higher resolution measurements are required to demonstrate the predicted discontinuity and change of sign of $\phi_q$ at the transition field $H_{c2}$.

A calculation of the Néel temperature as a function of magnetic field yields the following results, in the limit of weak applied fields:

$$T_N(H) = T_N(0) - m^2(c_1 + \tfrac{1}{4}c_2)\alpha_0 \,, \tag{4}$$

for $\mathbf{H}$ along $\langle 100 \rangle$ and

$$T_N(H) = T_N(0) - m^2 c_1/\alpha_0 \tag{5}$$

for $\mathbf{H}$ along $\langle \bar{1}20 \rangle$, where we assume

$$a(q_i) + a_1 q_i^2 = \alpha_0(T - T_N) \,.$$

In the first case, the Néel transition is to one of the two single-$q$ domains for which $\mathbf{q}_i$ does not lie along the particular $\langle 100 \rangle$ direction selected as the field direction, whereas in the second case the Néel transition is to the single-$q$ domain with its $\mathbf{q}_i$ perpendicular to the magnetic field direction. Measurements of the Néel temperature versus magnetic field in a $\langle 100 \rangle$ direction[9] (i.e., the upper phase boundary in Fig. 2) and in a $\langle \bar{1}20 \rangle$ direction[12] show that in both cases $T_N$ decreases with increasing magnetic field, the decrease being stronger for fields along $\langle 100 \rangle$. Thus $c_1$ and $c_2$ are both positive.

At sufficiently low temperatures, the sixth-order term $V_6 S_i^6 \cos(6\,\phi_s)$ arising from the crystalline electric field anisotropy within the basal plane, becomes significant. If the coefficient $V_6 < 0$, this term will tend to realign the spin components along the $\langle 100 \rangle$ directions at the expense of the $w_2 \sum_{i,j} (\mathbf{S}_i \cdot \mathbf{S}_j)^2$ term. As $\phi_s$ is reduced, so we expect $\phi_q$ to decrease: this effect is observed experimentally[6] between 14 and 6.4 K. It is interesting to note that in alloys of $\mathrm{Pr}_x\mathrm{Nd}_{1-x}$ for compositions where the average value of $V_6$ is close to zero, $\phi_q$ remains finite down to the lowest temperatures studied.[13]

In conclusion, the phenomenological free energy analysis developed here permits a consistent understanding of the magnetic phases of neodymium above 8 K, and of their magnetic field dependence, as revealed by recent neutron scattering and thermal expansion measurements. To elucidate fully the structure of the phases below 8 K which have been mapped out by the thermal expansion[9] and magnetization[14] studies, further neutron diffraction experiments are necessary.

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