Observation of a Quadruple-q Magnetic Structure in Neodymium

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Major progress has been made in understanding the complicated magnetic structures exhibited by dhcp neodymium metal. New evidence for the 2-**q** model of the structure between 19.1 and 9 K has been discovered in neutron-diffraction studies of intermodulation harmonics of the type $2\mathbf{q}_i \pm \mathbf{q}_j$. We have applied the same technique at 4.5 K and below. From an analysis of the harmonic combinations observed, we propose a new model for the lowest-temperature phase of Nd; it is characterized by a multidomain 4-**q** structure in which the magnitude and direction of each component wave vector is different.

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A detailed understanding of the sequence of magnetic structures exhibited by neodymium below $T_N = 19.9$ K has been an outstanding challenge in rare-earth magnetism for many years.[1-3] It now appears that the structure is single **q** immediately below T_N with a first-order transition at 19.1 K to a double-**q** structure.[4-6] The existence of the latter was demonstrated by McEwen *et al.*, who prepared a single domain by the application of a magnetic field.[7] They proposed that such a structure is present in zero field in a multidomain form: The neutron-diffraction patterns of the three possible domain orientations would then add to give the complicated pattern observed. In our measurements reported here, we have confirmed the existence of the double-**q** structure *in zero field* by the observation of its intermodulation harmonics. We have then applied this technique below 4.5 K to show that the extra modulation vectors present in this temperature region are coupled together to form a fascinating quadruple-**q** structure.

Near the Néel temperature, a given type of atomic site in the dhcp structure of neodymium will carry an average magnetic moment μ which varies with position **r** as

$$\mu(\mathbf{r}) = \sum_{i,\alpha} \mu_{i\alpha} \alpha \cos(\mathbf{q}_i \cdot \mathbf{r} + \phi_{i\alpha}) , \qquad (1)$$

where the sum on α is over the Cartesian directions x, y, and z, and the sum on i is over the number of **q**'s present simultaneously within a single domain. In neodymium the wave vectors are incommensurate with a length of about $0.13\tau_{100}$ above 9 K. We expect a multidomain single-**q** structure just below the Néel temperature and then a transition to a multidomain double-**q** state existing down to at least 9 K.

However, well below the Néel temperature, it is expected that any incommensurate magnetic structure would "square up" so as to increase the average value of the moment on each site. In a single-**q** structure, such a squaring up corresponds to the inclusion in Eq. (1) of harmonics which are odd multiples of the fundamental wave vector **q**, with the third harmonic at 3**q** as the strongest. In a multiple-**q** structure, the third-harmonic components may be a combination of any three fundamental wave vectors, i.e., not only at $3\mathbf{q}_i$, but also intermodulation harmonics at $2\mathbf{q}_i \pm \mathbf{q}_k$ and also at $\mathbf{q}_i \pm (\mathbf{q}_j \pm \mathbf{q}_k)$ for structures with three or more fundamentals. The existence of such harmonics was first pointed out by Moncton, Axe, and DiSalvo in their study[8] of the charge-density-wave structure of 2H-$TaSe_2$: they exist only if the component wave vectors are present in the same domain of the sample and will result in weak satellites in a neutron-diffraction pattern. Observation of intermodulation satellites thus gives an unambiguous indication of a multiple-**q** structure, even in a multidomain sample. This is illustrated in Fig. 1 which represents the diffraction pattern in the h-k plane around a typical reciprocal-lattice point for the dhcp structure. The positions of the fundamental wave vectors and the third harmonics expected from the double-**q** structure are indicated. Figure 1(b) shows the complete pattern resulting from three double-**q** domains. We note that other possible multiple-**q** structures could give the same pattern of fundamentals, but these would yield a different pattern of harmonics.

The Nd single crystal used for our experiments was of mass 0.6 g and had been prepared by a temperature-cycling technique[9] from a polycrystalline ingot of highest-purity start material, purchased from the Ames Laboratory.[10] Measurements were performed with the four-circle neutron diffractometer D10 at the Institut Laue-Langevin, Grenoble. The diffractometer was operated at a neutron wavelength of 2.36 Å; neutrons scattered elastically from the sample were detected after Bragg reflection from a pyrolytic graphite analyzer,

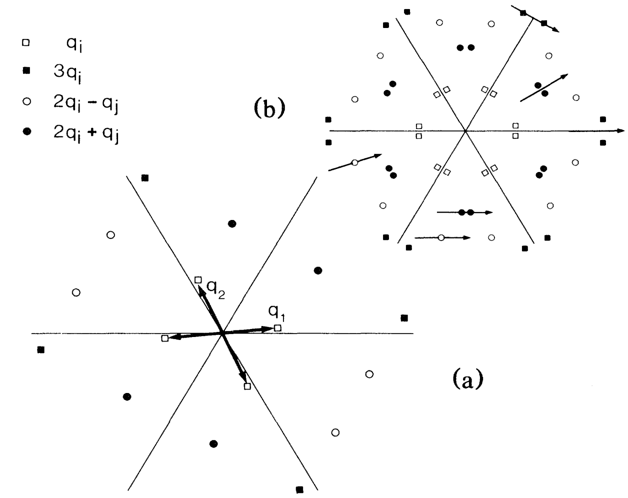

FIG. 1. (a) Schematic representation of neutron-diffraction satellites corresponding to the fundamental wave vectors in a single domain of the double-**q** structure: The symbols ■, ●, and ○ represent satellites arising from $3\mathbf{q}_i$, $2\mathbf{q}_i+\mathbf{q}_j$, and $2\mathbf{q}_i-\mathbf{q}_j$ harmonics, respectively. The axes drawn are the {100} directions. (b) Pattern of fundamentals and harmonics arising from all three domain orientations of the double-**q** structure of (a). The arrows represent scans about (003) performed in order to observe the positions and numbers of harmonics.

which reduced the background count rate. At a temperature of 10 K, scans were made through the harmonics around the (003) reciprocal-lattice point in the directions shown in Fig. 1. These scan directions were chosen to be close to the shortest axis of the resolution ellipsoid. In each case we indeed observed the third harmonics expected from the double-**q** structure. Accurate measurements of the positions of the intermodulation harmonics confirmed that the angle between the fundamental wave vectors was always slightly less than 120°. This suffices to rule out all alternatives to the double-**q** structure shown in Fig. 1. At 10 K the most intense harmonic (that at $2\mathbf{q}_1+\mathbf{q}_2$) had an intensity 0.6% of a fundamental. With increasing temperature, the intensities of the harmonics decreased approximately as the cube of the fundamental intensity.

Having confirmed the double-**q** structure above 10 K, we turned our attention to the changes in magnetic structure which begin on cooling through 8 K; at this temperature, additional magnetic ordering sets in,[11] with a modulation vector of length $\approx 0.18\tau_{100}$. Then, in a hysteretic transition taking place between 5 and 6 K, the directions of all the modulation vectors change.[12] The satellites of length $\approx 0.11\tau_{100}$ move to the {100} axes and split longitudinally; simultaneously, the satellites near $0.18\tau_{100}$ split into four.[13] In the low-temperature phase, a general reciprocal-lattice point is thus surrounded by the 36 magnetic satellites represented in Fig. 2. We have accurately determined the positions of these satellites at 4.5 K, and they are given in Table I.

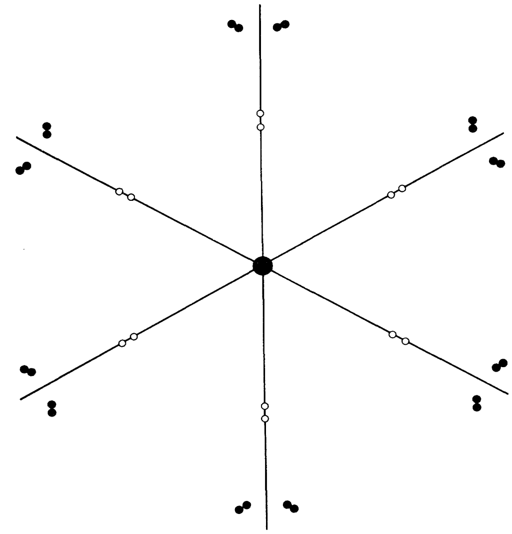

FIG. 2. Schematic representation of the satellites observed about a typical reciprocal-lattice point below 5 K. The symbols ○ and ● represent satellites around $0.11\tau_{100}$ and $0.18\tau_{100}$, respectively.

In analogy with the high-temperature phase, we expect that the satellite pattern of Fig. 2 arises from a multidomain multiple-**q** structure with each domain containing a basic set of modulation vectors. In order to determine the number of fundamental wave vectors, we searched at 4.5 K for harmonics around (003), scanning an area covering three 30° sectors of the $(h,k,3)$ plane. The existence of harmonics was confirmed, and their positions were accurately determined, by their appearance in each sector. A less complete survey was also carried out with a different cryostat able to maintain 1.6 K; additional harmonics became visible at that temperature. In Fig. 3(a) are represented the positions of a subset of the satellites observed. These have enabled us to prove the existence of domains containing four fundamentals in the relative orientations shown in Fig. 3(b). First, we

TABLE I. Values of modulation vectors observed in Nd at 4.5 K.

Vector	q_x [a]	$\lvert q_y \rvert$ [a]	h [b]	k [b]	h [c]	k [c]
$\mathbf{q}_1$	0.106	0.000	0.106	0.000	0.106	0.000
$\mathbf{q}_2$	0.116	0.000	0.116	0.000	−0.116	0.116
$\mathbf{q}_3$	0.181	0.013	0.173	0.015	0.015	0.173
$\mathbf{q}_4$	0.184	0.021	0.172	0.024	0.196	−0.172

[a]Cartesian components parallel and perpendicular to the nearest {100} direction.

[b]Components for an example of the vector close to (100).

[c]Components for each vector in the orientation shown in Fig. 3(b).

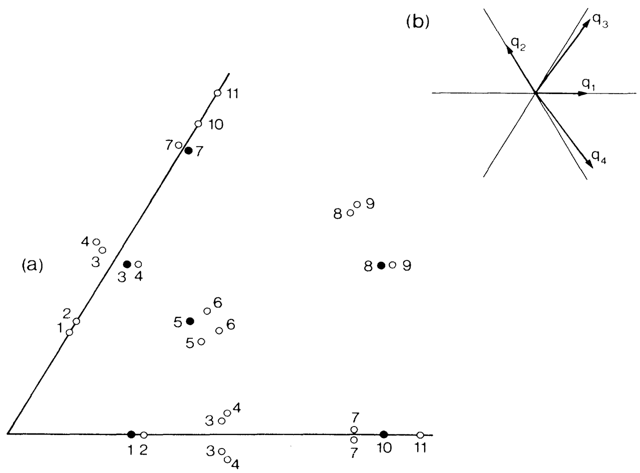

FIG. 3. A 60° sector of the $(h,k,3)$ plane showing a "diagnostic" set of the satellites that were observed. Those numbered 1–4 represent fundamental wave vectors and the others represent third harmonics, as described in the text. The satellites with filled symbols arise from the domain orientation in (b); those with open symbols arise from other domain orientations. (b) The relative orientations and lengths of the modulation vectors in a single domain of the quadruple-**q** structure which is prescribed by the harmonics shown in (a).

consider the harmonics numbered 5 and 6; these are intermodulation harmonics $2\mathbf{q}_1+\mathbf{q}_2$ and $2\mathbf{q}_2+\mathbf{q}_1$ [although some are from different domain orientations than that shown in Fig. 3(b)]. The position and number of these harmonics show that there is only one vector of length q_1 and one of q_2 in each domain and that they are always at 120° to each other. Thus, these wave vectors are still in a double-**q** type of structure, but one made up of two inequivalent vectors. Now we consider the harmonics labeled 7; they are of the form $\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3$ and their positions determine the orientation of $\mathbf{q}_3$ relative to $\mathbf{q}_1$ and $\mathbf{q}_2$. Finally, the very weak harmonics 8 (and 9, only visible at 1.6 K), which involve the combinations $2\mathbf{q}_3+\mathbf{q}_4$ and $2\mathbf{q}_4+\mathbf{q}_3$, determine the orientation of $\mathbf{q}_4$ in Fig. 3(b). We see that the fundamentals $\mathbf{q}_3$ and $\mathbf{q}_4$ of length $\approx 0.18\tau_{100}$ also form a second double-**q** structure locked in a specific orientation relative to the first. This quadruple-**q** structure leads to other harmonics in addition to those already discussed: We have identified another nine intermodulation harmonics in positions predicted by Fig. 3(b), as well as the harmonics labeled 11 and 12, which are at $3\mathbf{q}_1$ and $3\mathbf{q}_2$. The strongest harmonic, that at $3\mathbf{q}_1$, had an intensity 1.2% of its fundamental at 4.5 K. Further details will be published elsewhere.[14]

It may be asked what is the reason for the formation of this quadruple-**q** structure. Part of the answer is provided by the observation that within experimental error the following vector relationship holds:

$$\mathbf{q}_3+\mathbf{q}_4-2\mathbf{q}_1=\mathbf{0}. \qquad (2)$$

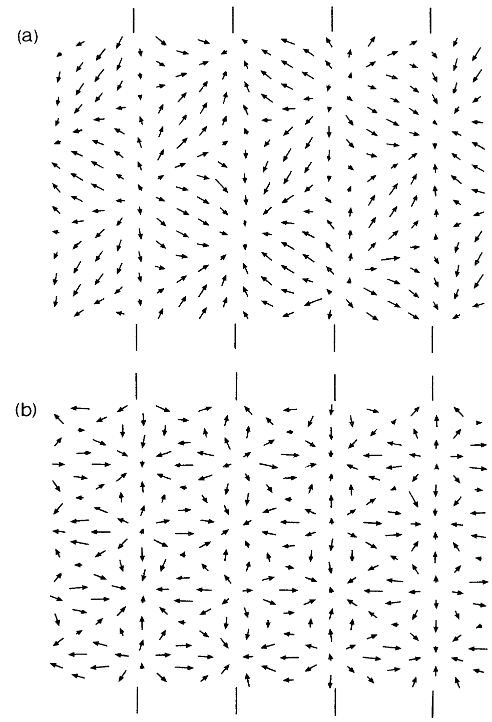

FIG. 4. A single layer of double-**q** structure formed: (a) from $\mathbf{q}_1$ and $\mathbf{q}_2$; (b) from $\mathbf{q}_3$ and $\mathbf{q}_4$. In each case, the extra lines represent a repeat distance corresponding to $2\mathbf{q}_1$.

We believe that this is not a coincidence, but that it is a necessary condition for the existence of a nonzero fourth-order term in the free energy of the form $\mu_3\mu_4\mu_1^2$ (μ_i being proportional to the amplitude of moment associated with $\mathbf{q}_i$). Such a term would provide the coupling energy necessary to lock together three of the four components of the quadruple-**q** structure. The relationship (2) may be seen in a direct way in the moment patterns of Fig. 4. These are calculated by the approximation that the moments associated with $\mathbf{q}_1$ and $\mathbf{q}_2$, and those with $\mathbf{q}_3$ and $\mathbf{q}_4$, are on different layers ("hexagonal" and "cubic,"respectively) of the dhcp lattice. This figure allows us to see the matching together of the two double-**q** patterns; however, the actual structure must have moments associated with all four **q** vectors in both layers.

In summary, we have shown that the low-temperature structure of neodymium is quadruple **q** with four inequivalent wave vectors, which can be regarded as a coupling of two closely related pairs. Although we have not observed all the harmonics predicted from the proposed structure (some are presumably too weak), the intermodulation harmonics observed are sufficient to prescribe the relative orientations of the wave vectors involved. In a multidomain sample, six orientations of this structure may be found, and the observed diffraction pattern is a superposition of them. Some interesting questions still remain: It is not clear why the shorter modulation vectors $\mathbf{q}_1$ and $\mathbf{q}_2$ move very close to the {100} axes when this structure is formed: There is no symmetry requirement that this should occur. In addition, the detailed nature of the ordering between 6 and 8.3 K is still open to question. Unfortunately, in this temperature region, the harmonics involving the longer modulation vectors are exceedingly weak and have not yet been detected.

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[10]Major impurities: other rare earths: 15 ppma; Fe: 10 ppma; Si: 10 ppma; O: 522 ppma; n: 125 ppma; C: 96 ppma.

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