Magnetism in neodymium at high pressure

1996 J. Phys.: Condens. Matter 8 5049

(http://iopscience.iop.org/0953-8984/8/27/014)

J. Phys.: Condens. Matter **8** (1996) 5049–5057. Printed in the UK

Magnetism in neodymium at high pressure*

D Watson†, E M Forgan†, W J Nuttall‡, P E Sokol§, S J Shaikh†, S W Zochowski‖ and D Fort¶

† School of Physics and Space Research, University of Birmingham, Birmingham B15 2TT, UK
‡ Department of Physics, Keele University, Keele, Staffs ST5 5BG, UK
§ Department of Physics, 104 Davey Laboratory, The Pennsylvania State University, University Park, PA 16802, USA
‖ Department of Physics, Birkbeck College, University of London, Malet Street, London WC1E 7HX, UK
¶ School of Metallurgy and Materials, University of Birmingham, Birmingham B15 2TT, UK

Received 15 March 1996, in final form 8 May 1996

Abstract. We have carried out magnetic neutron diffraction studies of a single crystal of neodymium at high pressure, using clamp cells on the diffractometer D10 at the Institut Laue–Langevin, Grenoble. The magnetic ordering was investigated at pressures up to 14 kbar in the temperature range 1.4–25 K. A number of quite different magnetic phases were observed, including the coexistence of ferromagnetic and antiferromagnetic ordering of moments on the inequivalent crystallographic sites. The structures formed and the population of the different symmetrically equivalent domains appear to be affected by complex interactions between the cubic-site ferromagnetism, the antiferromagnetic hexagonal-site ordering and a uniaxial component of stress.

1. Introduction

The crystal structure of neodymium is double-hexagonal close packed, dhcp. Ions are arranged in close-packed layers, stacked along the $\boldsymbol{c}$-axis in the sequence ABAC. Ions in layers B and C have nearest neighbours arranged as they would be in a hexagonal close-packed structure. The nearest neighbours of ions in the layers labelled A are arranged with near-cubic symmetry. These different sites are known as 'hexagonal' and 'cubic' respectively. Ions in these inequivalent sites experience different crystal fields and exchange interactions. This affects the resulting magnetic order which differs between the two sites.

The magnetic phases of pure neodymium in the absence of applied pressure are well known to be a series of antiferromagnetic sinusoidal modulations [1–7]. In such structures the average magnetic moment $\boldsymbol{\mu}_s$ on a given type of site (s = 'hexagonal' or 'cubic') at position $\boldsymbol{r}$ will be

$$\boldsymbol{\mu}_s(\boldsymbol{r}) = \sum_{i,\alpha} \mu_{s,i,\alpha} \hat{\boldsymbol{\alpha}} \cos(\boldsymbol{q}_i \cdot \boldsymbol{r} + \phi_{s,i,\alpha})$$

where $\mu_{s,i,\alpha}$ is the magnitude of the moment in the Cartesian direction $\hat{\boldsymbol{\alpha}} = \hat{\boldsymbol{x}}, \hat{\boldsymbol{y}}, \hat{\boldsymbol{z}}$, associated with the ith modulation vector $\boldsymbol{q}_i$. On cooling below the Néel temperature of 19.9 K there is initial ordering of moments mainly on the hexagonal sites, and in each domain only one $\boldsymbol{q}$-vector is present in the sum above. This is known as a 1-$\boldsymbol{q}$ structure.

* Neutron diffraction work was carried out at the Institut Laue–Langevin, Grenoble, France.

0953-8984/96/275049+09$19.50

This phase persists for only $\leqslant$1 K before a 2-$\boldsymbol{q}$ structure forms. Below 8.3 K a series of phase transitions occurs associated with ordering predominantly on the cubic sites and the number of modulation vectors increases to four below $\sim$6 K [3]. All of the zero-pressure phases are antiferromagnetic and all of the modulation wavevectors are along or close to {100}-type directions†. The modulation vectors associated with the 'hexagonal' ordering tend to be reasonably well aligned with the corresponding magnetic moments [5, 8].

The application of pressure to rare-earth metals causes them to adopt crystal structures appropriate to lighter rare earths [9]. If this also applies to magnetic structures then application of pressure should have similar effects to alloying with lighter rare earths. The magnetic structures of $Nd_{1-x}Ce_x$ alloys have been investigated [10]. Quite small fractions of Ce are found to induce ferromagnetic ordering, mainly on the cubic sites, while incommensurate antiferromagnetic order remains, but mainly on the hexagonal sites. The ferromagnetic moments lie along the (001) direction. Investigations into the effect of pressure on $Nd_{0.9}Ce_{0.1}$ [11] show that increasing the pressure has qualitatively similar effects to increasing the Ce concentration, with the ferromagnetic ordering temperature, T_C, increasing as the pressure is increased.

Alloys of Nd with light rare earths, Pr [12–14] and La [15], also exhibit ferromagnetic order, with moments along (001) mainly on the cubic sites. The hexagonal sites remain mainly incommensurately antiferromagnetic. Yttrium behaves like a non-magnetic heavy rare earth: there was no sign of ferromagnetism in a low-yttrium-concentration Nd–Y alloy [13].

Uniaxial stress applied along the ($\bar{1}$20) direction of pure Nd has been shown to affect the populations of the different magnetic domains in the 2-$\boldsymbol{q}$ phase [16]. Application of 1 kbar was enough to suppress completely those magnetic domains with moments nearly perpendicular to the stress. Any non-hydrostatic component of stress in our pressure cell may be expected to have a similar effect.

The presence of ferromagnetism may have effects analogous to the application of a magnetic field. McEwen *et al* [4] showed that low fields nearly parallel to (100) alter the 2-$\boldsymbol{q}$ phase by favouring domains that have moments nearest to perpendicular to the field. We may therefore expect a similar correlation between the local directions of ferromagnetic moments and antiferromagnetic moments. It was also shown that applied fields over 3 T caused the formation of a 1-$\boldsymbol{q}$ structure where the modulation vector and associated modulated moment were almost perpendicular to the field. The development of suitably large ferromagnetic moments on the cubic sites may also be expected to force the formation of 1-$\boldsymbol{q}$ ordering of the hexagonal sites.

2. Experimental details

The neutron diffraction experiments were performed on diffractometer D10 at the Institut Laue–Langevin, Grenoble with a wavelength of 2.36 Å. A pyrolitic graphite filter was used to prevent contamination by neutrons with half this wavelength. A single crystal of neodymium, grown by the solid-state strain anneal method at elevated temperatures in UHV [17], was placed inside a high-pressure clamp cell [18] surrounded by a fluorocarbon, Fluorinert (C_8F_{18}). Liquid at room temperature and ambient pressure, the Fluorinert solidifies at the low temperatures of our experiment; this may introduce a uniaxial component

† In all of this paper the symbol (hkl) represents a vector in reciprocal space perpendicular to the (hkl) planes. Since in Nd there is strong coupling between moment directions and $\boldsymbol{q}$-vectors, we shall denote all directions by their (hkl) symbols; {100} represents the set of vectors which are symmetry related to (100).

of stress along the cylindrical axis of the clamp cell. Inside the pressure cell with the Nd was a crystal of NaCl which was used to determine the pressure at low temperatures using the well known pressure and temperature dependencies of the lattice parameter of NaCl [19].

Pressure was applied at room temperature; the cell was clamped and then loaded into a variable-temperature cryostat. Temperatures were measured to an accuracy of 0.1 K by carbon thermometers in the cryostat which were subsequently calibrated against a standard Ge thermometer. Care was taken to allow time for the clamp cell to reach thermal equilibrium.

The cryostat was mounted on the diffractometer so that the axis of the clamp cell was approximately vertical and the horizontal scattering plane contained the (100) and (001) directions of the Nd crystal. This plane allowed investigation of antiferromagnetic satellites of (00ℓ) and the possible observation of ferromagnetic scattering at (00ℓ) and (100). Scattering vectors slightly out of the $(h0\ell)$ plane were attainable by tilting the cryostat. The NaCl crystal was arranged so that two of the {100}-type directions were in the scattering plane, and the third was vertical.

After cooling to 2 K, the lattice parameter of the NaCl was found by measuring various nuclear peaks in the horizontal scattering plane. For this, the graphite filter was removed to increase the number of peaks available by observation of diffraction of neutrons with half the normal wavelength. The pressures were then determined to an accuracy of 0.5 kbar using the data tabulated by Skelton *et al* [19], neglecting the effects of any uniaxial component of stress. It was determined that the diffraction measurements were made at four elevated pressures, 2.1, 8.2, 11.6 and 13.8 kbar. Rocking curves through (004) for Nd at 11.6 and 13.8 kbar gave mosaic spreads of 0.29° and 0.40° respectively; these were somewhat degraded from the 0.23° observed before the application of pressure.

Antiferromagnetic order with modulation vector $\boldsymbol{q}$ will lead to magnetic diffraction satellites displaced from reciprocal-lattice points by $\pm\boldsymbol{q}$. The hexagonal symmetry of the basal plane of neodymium means there are six distinct symmetry-related directions in which a general basal-plane $\boldsymbol{q}$-vector can point and hence twelve directions of $\pm\boldsymbol{q}$. In different domains of the sample, the vector is likely to be pointing in each of the possible directions, leading to the presence of a maximum of twelve magnetic satellites around a reciprocal-lattice point in a multidomain sample. The symmetrical equivalence of the domain orientations can be broken, for example by a magnetic field or uniaxial stress. This can reduce the number of domains present and therefore the number of satellites that appear. For example, in a single-domain 2-$\boldsymbol{q}$ sample [7] only two modulation vectors will be present, each producing two satellites at $\pm\boldsymbol{q}$.

Searches were made for satellites of reciprocal-lattice points of the type (00ℓ) along and in the vicinity of the (100), (010) and $(\bar{1}10)$ directions, as shown in figure 1. The satellite intensities as a function of temperature were measured by scanning in the (100) direction. The resolution of our experimental arrangement was such that we did not expect to resolve two closely spaced satellites either side of a {100}-type direction, if they were present, as for example those produced by a multidomain sample with the zero-pressure 2-$\boldsymbol{q}$ structure.

For scattering at (002), a forbidden nuclear peak, the magnetic structure factor is $2\boldsymbol{\mu}_c - 2\boldsymbol{\mu}_h$, where $\boldsymbol{\mu}_c$ and $\boldsymbol{\mu}_h$ represent the moments on ions in the cubic and hexagonal sites respectively. Any scattering at the (002) position must therefore arise from unequal amounts of ferromagnetic ordering on the different sites. In general, ferromagnetic ordering will also contribute to scattering at (100), an allowed nuclear peak, where the magnetic structure factor is $2\boldsymbol{\mu}_c - \boldsymbol{\mu}_h$. The intensities at (100) and (002) were monitored as a function of temperature by scans in the (100) and (001) directions respectively. In the cross-section for coherent elastic scattering of neutrons by periodically ordered moments the square of the

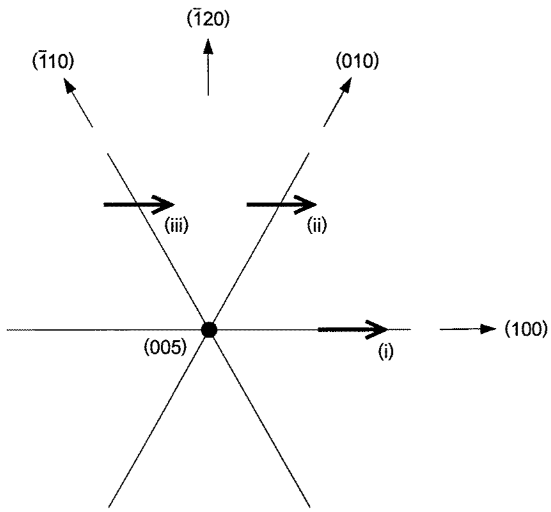

Figure 1. Geometry of scans in the basal plane around (005). The arrows labelled (i), (ii) and (iii) represent scans in the (100) direction through possible satellite positions, $(q05)$, $(0q5)$ and $(\bar{q}q5)$ respectively.

magnetic structure factor appears, multiplied by the moment orientation factor, $1-(\hat{\mu}\cdot\hat{k})^2$, where $\hat{\mu}$ and $\hat{k}$ represent unit vectors in the direction of the magnetic moment and the scattering vector respectively. The relative intensities of magnetic scattering at (100) and (002) are controlled by the moment orientation factor so they will give some information regarding the direction of the ordered moments.

3. Results

3.1. 2.1 and 8.2 kbar

Measurements at 2.1 kbar indicated no significant changes from the magnetic structures seen with no applied pressure in this experiment and earlier work. All of the various multi-$\boldsymbol{q}$ antiferromagnetic phases were present, with no noticeable difference in the ordering temperatures. There was no sign of ferromagnetic scattering at either (100) or (002).

Application of 8.2 kbar produced a major change. The highest Néel temperature of 19.9 K was not affected by the pressure, but the lowest-temperature phase seen at ambient pressure, 4-$\boldsymbol{q}$ antiferromagnetism, was not observed. However, at base temperature, satellites arising from antiferromagnetic order on both the hexagonal and cubic sites were present.

Scattering at (002) and an increase in the (100) intensity indicated that ferromagnetic order was also present below an ordering temperature of 12 K. This ordering was likely to have been mainly on the cubic sites, because the hexagonal sites had already ordered antiferromagnetically at 19.9 K.

The presence of both antiferromagnetism and ferromagnetism on the cubic sites suggests that the magnetic structure varied throughout the crystal volume. This coexistence of two phases indicates that the pressure in the crystal may not have been uniform and that the phase boundary falls at approximately 8 kbar.

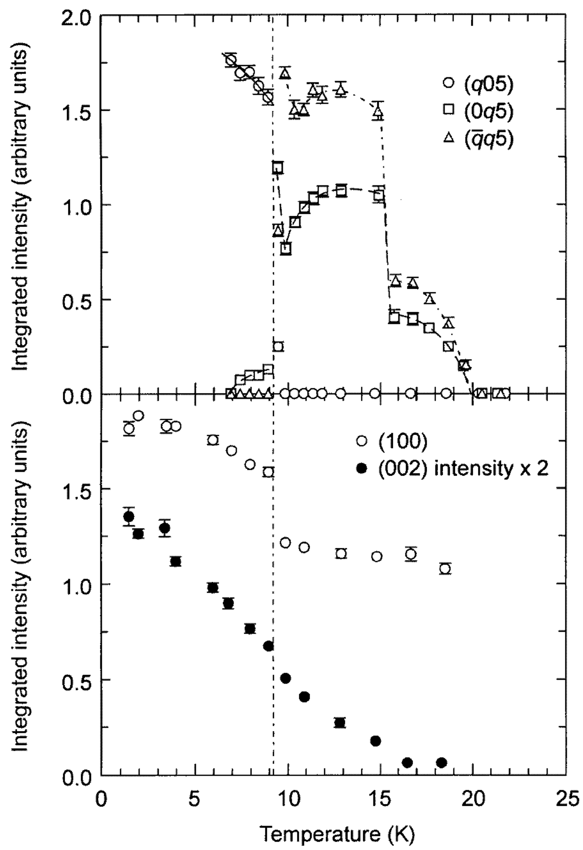

Figure 2. Integrated intensities of various diffraction peaks at 11.6 kbar. The top panel shows the intensities of three satellites of (005), arising from incommensurate antiferromagnetic order mainly on the hexagonal sites. The lines through the points are intended as a guide to the eye. The intensities in the lower panel are of (100) and (002). The (002) intensity arises from ferromagnetic order—it is a forbidden nuclear peak. The (100) intensity is an allowed nuclear peak with an extra contribution from ferromagnetism. Note that the intensity units on the different panels are not the same.

3.2. 11.6 kbar

The main results of our investigation at 11.6 kbar are shown in figure 2. This shows how the intensities of (100), (002) and satellites of (005) varied as a function of temperature. The data shown were taken on heating; data taken on cooling were very similar.

The Néel temperature appears to be unchanged from the zero-pressure value of 19.9 K. A similar lack of sensitivity to pressure was reported for a $Nd_{0.9}Ce_{0.1}$ alloy [11]. Just below this temperature, satellites appear along (010) and ($\bar{1}$10), but not (100). These satellites correspond to $\boldsymbol{q}$-vectors of length $\sim 0.130\tau_{100}$, similar to the $\boldsymbol{q}$-vectors in the zero-pressure 2-$\boldsymbol{q}$ phase [7]. On cooling, the lengths decrease to $\sim 0.115\tau_{100}$ at 10 K. We attribute these satellites to 2-$\boldsymbol{q}$ antiferromagnetic ordering on the hexagonal sites, while the cubic sites remain disordered, except for small moments induced by the hexagonal-site ordering [2].

We note that between 9.4 and 19.9 K there is no satellite along (100), so not all of the antiferromagnetic domains are equally occupied. We attribute this to a uniaxial component of stress along $(\bar{1}20)$, i.e. parallel to the axis of the pressure cell and perpendicular to the scattering plane. The effect of stress in this direction has been shown to suppress modulations whose moments are nearly perpendicular to $(\bar{1}20)$ [16].

There is a sudden increase in the intensity of the antiferromagnetic satellites on cooling through 15.3 K. This appears to be correlated with the onset of ferromagnetic ordering on the cubic sites, indicated by the scattering appearing at (002), but the cause of this intensity change is not understood. It is not associated with any sudden changes in the position or width of the satellite peaks. Between 18.5 and 9.4 K the intensity of (100) remained constant to within experimental uncertainty. This would be the case if the moments associated with the ferromagnetism on the cubic sites are pointing along a direction parallel to (100), or close to this direction, possibly (110). The moment orientation factor for scattering at (100) is zero if $\hat{\boldsymbol{\mu}}$ is parallel to (100) and 0.25 if $\hat{\boldsymbol{\mu}}$ is along (110). The factor will equal 1 for any $\hat{\boldsymbol{\mu}}$ in the basal plane for scattering at (002).

If the interaction between the ferromagnetism and the antiferromagnetic moments is similar to that seen between antiferromagnetism and an external magnetic field [4], this moment direction can be explained. McEwen *et al* showed that a magnetic field along (100) enhanced those antiferromagnetic modulations whose wavevectors are nearly perpendicular to the field direction. In our experiment the interaction presumably works the other way round; the pre-existence of only certain antiferromagnetic modulations encourages a specific orientation for the ferromagnetic order.

At around 9.4 K the intensity of (100) suddenly changes but that of (002) does not. The simplest interpretation of this is that the ferromagnetic moments rotate *within* the basal plane with unchanged magnitude. A ferromagnetic moment direction of $(\bar{1}20)$ would give similar magnetic intensities at (002) and (100), as is observed. The magnitude of the ferromagnetic moment can be estimated from the change in intensity of the (100) peak. Assuming that the moment is along $(\bar{1}20)$ and is entirely on the cubic sites, and that the (100) peak is not strongly affected by extinction, we obtain $1.2\mu_B$ per cubic site. This is comparable with the cubic site moments observed in $Nd_{1-x}Ce_x$ alloys [10].

Also at 9.4 K there is a dramatic change in the antiferromagnetic hexagonal-site ordering. Below this temperature only satellites along (100) are present, in complete contrast to the situation above 9.4 K. The antiferromagnetic structure appears to be 1-$\boldsymbol{q}$ and single domain. We can understand this as an increasing ferromagnetic moment acting in a similar way to a larger magnetic field and forcing the hexagonal-site antiferromagnetism into a 1-$\boldsymbol{q}$ structure as reported by McEwen *et al* [4].

It appears that below 9.4 K the most important interaction determining moment direction and domain population is that between the ferromagnetic moments and the uniaxial stress. If stress along the clamp cell axis favours ferromagnetic moments along $(\bar{1}20)$ relative to any otherwise equivalent direction, then the 1-$\boldsymbol{q}$ hexagonal-site ordering would have wavevectors, and presumably magnetic moments, along (100) because the ferromagnetism has similar effects to an applied magnetic field along $(\bar{1}20)$.

3.3. 13.8 kbar

Figure 3 shows the results taken at the highest pressure, 13.8 kbar. Again the antiferromagnetic domain populations and ferromagnetic moment direction are temperature dependent. The data presented were taken on heating; as was the case at 11.6 kbar, data taken on cooling were very similar.

An important difference between the results at the two high pressures is the relative values of the antiferromagnetic and ferromagnetic ordering temperatures, T_N and T_C

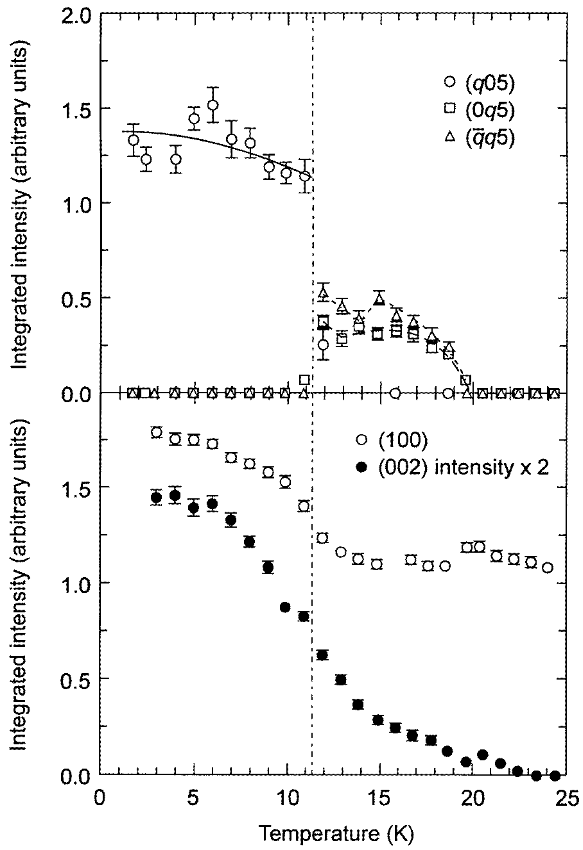

Figure 3. Integrated intensities of various diffraction peaks at 13.8 kbar. The top panel shows the intensities of three satellites of (005), arising from incommensurate antiferromagnetic order mainly on the hexagonal sites. The lines through the points are intended as a guide to the eye. The intensities in the lower panel are of (100) and (002). The (002) intensity arises from ferromagnetic order—it is a forbidden nuclear peak. The (100) intensity is an allowed nuclear peak with an extra contribution from ferromagnetism. Note that the intensity units for the different panels are not the same.

respectively. The value of T_N still appears unaffected by the pressure; however, T_C has increased to 21.5 K, above T_N. The magnitude of the ordered moment is little altered.

The ferromagnetism appears to have ordered into a similar orientation to that adopted at 11.6 kbar, with the moments along a direction near (100). The evidence for this is the constant (100) intensity, ignoring statistical fluctuations, and the increasing (002) intensity on cooling from 21.5 to 14 K. The hexagonal-site antiferromagnetism takes the same structure as seen at 11.6 kbar, a 2-$\boldsymbol{q}$ structure with only those satellites along (010) and ($\bar{1}$10) having measurable intensity.

There is a transition at 11.3 K, whose nature appears to be similar to the 9.4 K transition at 11.6 kbar. This can be explained if the ferromagnetic moment again rotates to point along ($\bar{1}$20); again 1-$\boldsymbol{q}$ antiferromagnetism is present below 11.3 K. The change in the (100) intensity is less sudden than seen earlier. A preliminary phase diagram summarizing all of these results is shown as figure 4.

With no applied pressure there is a 1-$\boldsymbol{q}$ phase that exists in a very small temperature

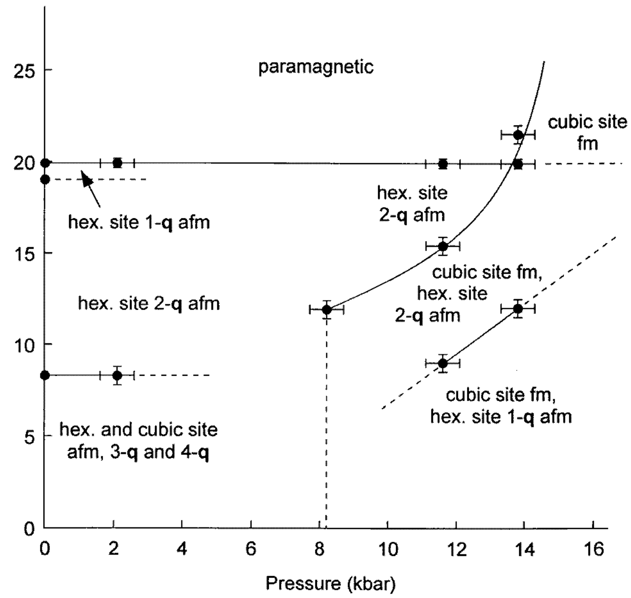

Figure 4. The magnetic phase diagram of Nd under pressure. The abbreviations 'fm' and 'afm' refer to ferromagnetism and antiferromagnetism respectively. Where hexagonal or cubic sites are not mentioned they are disordered.

range immediately below the Néel temperature. We have no evidence at present for the high-temperature 1-$\boldsymbol{q}$/2-$\boldsymbol{q}$ transition under pressure, though it presumably still occurs [20], in which case at higher pressures this transition is re-entrant.

4. Summary

We have reported the effects of high pressure on the magnetic ordering of neodymium. Magnetic phases have been identified that consist of antiferromagnetism, ferromagnetism, and the coexistence of both types of order. The different ordering occurs predominantly on the different crystallographic sites in the dhcp unit cell. The temperature dependence of the pattern of satellites produced by antiferromagnetic order and the observed ferromagnetic scattering intensities suggest that there are interactions between the different types of ordering and a uniaxial component of stress. The ferromagnetic moment interacts with the antiferromagnetic order in a similar way to a magnetic field applied along the same direction [4]; small ferromagnetic moments adopt a preferred orientation with respect to the 2-$\boldsymbol{q}$ antiferromagnetic order present mainly on the hexagonal sites; larger moments force the antiferromagnetism into a 1-$\boldsymbol{q}$ structure. It is of interest that the same RKKY interaction can cause antiferromagnetic order on one site and ferromagnetism on the other site.

We look forward to continuing this work, and we anticipate that many other interesting results can be achieved by investigating other pressures both in the central region of figure 4 and at pressures above 14 kbar.

Acknowledgments

We would like to acknowledge the invaluable assistance of G J McIntyre and L Melesi at the ILL. We thank the EPSRC for financial assistance.

References

[1] Moon R M, Cable J W and Koehler W C 1964 *J. Appl. Phys.* **35** 1041
[2] Lebech B 1981 *J. Appl. Phys.* **52** 2019
[3] Forgan E M, Gibbons E P, McEwen K A and Fort D 1989 *Phys. Rev. Lett.* **62** 470
[4] McEwen K A, Forgan E M, Stanley H B, Bouillot J and Fort D 1985 *Physica* B **130** 360
[5] Forgan E M, Lee S L, Marshall W G and Fort D 1992 *J. Magn. Magn. Mater.* **104–107** 913
[6] Zochowski S W, McEwen K A and Fawcett E 1991 *J. Phys.: Condens. Matter* **3** 8079
[7] Watson D, Forgan E M, Nuttall W J, Stirling W G and Fort D 1996 *Phys. Rev.* B **53** 726
[8] Gibbons E P, Forgan E M, Lee S L, McEwen K A, Marshall W G and Fort D 1992 *Physica* B **180+181** 91–3
[9] Gschneidner K A Jr and Calderwood F W 1986 *Handbook of the Physics and Chemistry of Rare Earths* vol 8 (Oxford: North-Holland) p 156
[10] Gibbons E P, Forgan E M and McEwen K A 1989 *Physica* B **156+157** 774
[11] Forgan E M, Shaikh S J, Fort D, Zochowski S and Vettier C 1992 *J. Magn. Magn. Mater.* **104–107** 1521
[12] McEwen K A, Lebech B and Fort D 1986 *J. Magn. Magn. Mater.* **54–57** 457
[13] Zochowski S W, Marshall W G, McEwen K A, Forgan E M, Fort D and Shaikh S 1992 *Physica* B **180+181** 26
[14] Boghosian H H and Coles B R 1985 *Phil. Mag.* B **52** 579
[15] Forgan E M, Lee S L, Marshall W G and Zochowski S 1992 *J. Magn. Magn. Mater.* **104–107** 1519
[16] McEwen K A, Vettier C and Lebech B 1983 *J. Magn. Magn. Mater.* **31–34** 171
[17] Fort D 1987 *J. Less Common Met.* **134** 45
[18] Gobrecht K, Melesi L and McIntyre G J 1992 *ILL Technical Report* 92GO04T
[19] Skelton E F, Webb A W, Qadri S B, Wolf S A, Lacoe R C, Feldman J L, Elam W T, Carpenter E R Jr and Huang C Y 1984 *Rev. Sci. Instrum.* **55** 849
[20] Zochowski S and McEwen K A 1986 *J. Magn. Magn. Mater.* **54–57** 515