"Triple-$\vec{q}$" Modulated Magnetic Structure and Critical Behavior of Neodymium

Per Bak
Nordita, DK-2100 Copenhagen, Denmark

and

Bente Lebech
Physics Department, Risø National Laboratory, DK-4000 Roskilde, Denmark

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We have determined the magnetic structure of neodymium metal by combining the results of neutron diffraction studies on single crystals of neodymium with the results of Landau symmetry arguments and renormalization-group theory. The spins form a unique, two-dimensional, incommensurably modulated structure accompanied by a similarly modulated lattice distortion. The experimental value of the critical exponent $\beta = 0.36 \pm 0.02$ is in agreement with the theoretical prediction of $\beta \sim 0.38$.

The magnetic structure of the rare-earth metal neodymium has remained a mystery for more than a decade. Detailed neutron diffraction measurements have been available, but no model proposed so far has been able to fit the data satisfactorily. In this Letter we report a solution to this problem. We have performed neutron scattering measurements on single crystals of neodymium and combined the experimental data with the results of Landau and renormalization-group theory. The magnetic structure below the Néel temperature was found to be a fascinating two-dimensionally ordered structure not observed in any other system. The magnetic ordering is accompanied by a lattice distortion which forms a similar pattern.

The crystal structure of neodymium is hexagonal with stacking sequence $ABA'C$ (dhcp) along the c axis ($\hat{z}$). Moon, Cable, and Koehler[1] reported the first neutron scattering data on neodymium. They found satellites in the elastic spectrum displaced from reciprocal-lattice points ($\vec{\tau}$) by vectors $\pm\vec{q}_1$, $\pm\vec{q}_2$, and $\pm\vec{q}_3$ in the three equivalent $\hat{b}_1$ directions. They proposed a model for the incipient magnetic ordering that persists down to ~7.5 K.[1,2] In this model *only* the spins in the B and C layers order as described by $\vec{\mu}_B(\vec{r}) = -\vec{\mu}_C(\vec{r}) = \mu_h \hat{b}_1 \times \cos(\vec{q}\cdot\vec{r})$. As pointed out already in Ref. 1 this model has several inadequacies. Most important, it predicts zero intensities of satellites on the $\hat{b}_1$ axes and identical intensities of satellites at $\vec{\tau} + \vec{q}_1$ and $\vec{\tau} - \vec{q}_1$. Small, but finite intensities were, however, observed on the $\hat{b}_1$ axes, and likewise, different intensities were observed for satellites at $\vec{\tau} + \vec{q}_1$ and at $\vec{\tau} - \vec{q}_1$. Our neutron diffraction measurements, performed at the steady-state reactor DR3 at Risø at 10 K on single crystals of neodymium, agree with the results described by Moon, Cable, and Koehler.[1] In addition, we studied the temperature dependence of selected satellites near T_N.

From the temperature dependences of $\{q, 0, l\}$ satellite intensities, we conclude that the transition at T_N is of *second order* (Fig. 1). According to one of the Landau rules, the symmetry-breaking order parameter should then transform as an irreducible representation of the space group of

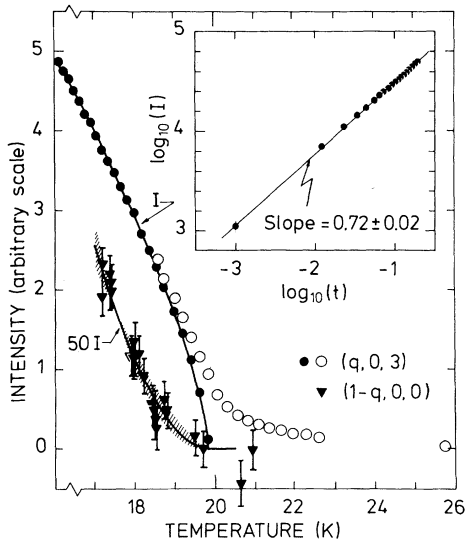

FIG. 1. Temperature dependences of the neutron intensities of the structural satellite $(1-q,0,0)$ and the magnetic satellite $(q,0,3)$. The solid lines are the results of least-squares fits to power laws as described in the text. The hatched area corresponds to a 25% variation of the exponent describing the temperature dependence of the $(1-q,0,0)$ structural satellite. The unfilled circles show the $(q,0,3)$ intensities before subtraction of the critical intensities. The inset shows a log-log plot of the $(q,0,3)$ Bragg intensities versus reduced temperature, t.

the paramagnetic phase.[3] The star of $\vec{q}_1$ consists of the *six* equivalent basal-plane vectors, $\pm\vec{q}_1 = \pm(q, 0, \bar{q}, 0)$, $\pm\vec{q}_2 = \pm(0, q, \bar{q}, 0)$, and $\vec{q}_3 = \pm(q, \bar{q}, 0, 0)$, where q varies from ~ 0.144 at $T_N = 19.9$ K to $q \sim 0.125$ at $T \sim 7.5$ K in an apparently continuous way. The point group which leaves $\vec{q}_1$ invariant is C_{2v}. This group has four *one*-dimensional representations, so that the order parameter describing the phase transition has $n = 6 \times 1$ components. The only representation of C_{2v} which is consistent with a magnetic moment along $\vec{q}_1$ in the B and C planes is A_2. The six components of the order parameter are denoted $\psi(\pm\vec{q}_k) = M_k \times \exp(\pm i\alpha_k)$, where $k = 1, 2, 3$. The most general structure described by the order parameters M_k and α_k are linear combinations of the terms

$$\begin{aligned}
\vec{\mu}_A{}^k(\vec{r}) &= (\mu_c \hat{q}_k - \mu_z \hat{z}) \cos(\vec{q}_k \cdot \vec{r} + \alpha_k), \\
\vec{\mu}_{A'}{}^k(\vec{r}) &= (\mu_c \hat{q}_k + \mu_z \hat{z}) \cos(\vec{q}_k \cdot \vec{r} + \alpha_k), \\
\vec{\mu}_B{}^k(\vec{r}) &= \mu_h \hat{q}_k \cos(\vec{q}_k \cdot \vec{r} + \tfrac{1}{2}\theta + \alpha_k), \\
\vec{\mu}_C{}^k(\vec{r}) &= \mu_h \hat{q}_k \cos(\vec{q}_k \cdot \vec{r} - \tfrac{1}{2}\theta + \alpha_k).
\end{aligned} \tag{1}$$

The parameters μ_c, μ_h, μ_z, and θ must be determined experimentally. In Landau theory, the free energy is expanded in terms of the components of the order parameter:

$$F = r\sum_k M_k{}^2 + u\sum_k M_k{}^4 + v \sum_{k>j} M_k{}^2 M_j{}^2, \tag{2}$$

where $r \sim T - T_N$. This expansion is formally identical to the one found by Krinsky and Mukamel[4] with $M_k{}^2 = \varphi_k{}^2 + \bar{\varphi}_k{}^2$. By minimizing F, we find that the "phase diagram" consists of three different regions, separated by the heavy lines in Fig. 2: (I) $0 < 2u < v$: second-order transition. The ordered state has *either* M_1, M_2, or $M_3 \neq 0$ ("*single*-$\vec{q}$" structure). By choosing $\mu_c = \mu_z = 0$ and $\theta = 180°$, we obtain the structure of Moon, Cable, and Koehler.[1] (II) $v < 2u$ and $u + 2v > 0$: second-order transition. In the ordered state, $M_1 = M_2 = M_3 \neq 0$, i.e., the three different equivalent $\vec{q}$ vectors are present simultaneously ("*triple*-$\vec{q}$" structure). (III) $u < 0$ or $u + v > 0$: first-order transition.

In the critical region, Landau theory is insufficient. Wilson and Fisher's theory[5] extends the Landau theory by taking into account fluctuations in the order parameter in $d = 4 - \epsilon$ dimensions. Near the phase transition, the coefficients u and v should be replaced by renormalized values obtained by repeated applications of the renormalization group transformation. At a second-order transition, u and v should converge to a stable fixed point.

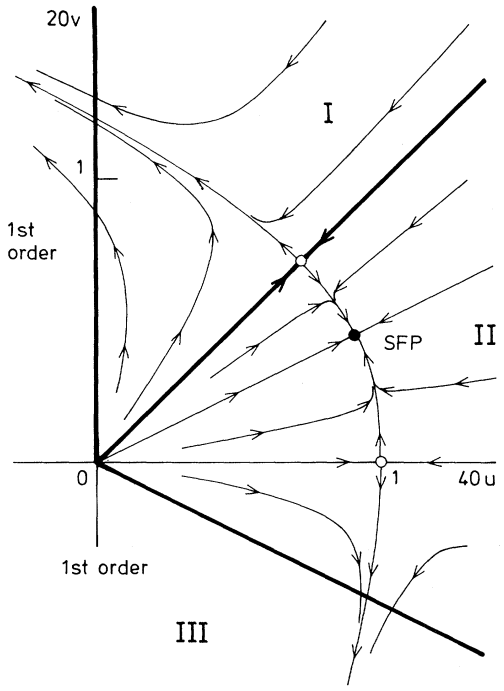

FIG. 2. Renormalization-group flow diagram for the coupling constants u and v defined in the text. SFP (○) is the only stable fixed point and corresponds to a second-order phase transition at T_N. The unfilled circles correspond to unstable fixed points.

The flow diagram for the recursion relations of u and v is also shown in Fig. 2, correct to order ϵ. The striking feature of the diagram is that, if the initial Hamiltonian is in region I, the Hamiltonian is unstable and the flow carries u and v into the *first-order* region. A first-order transition is therefore expected according to the "fourth Landau rule" proposed by Bak, Mukamel, and Krinsky.[6] The flow converges to the stable anisotropic fixed point (SFP) only if the initial Hamiltonian is in the $v > 0$ part of region II. Since this fixed point is in region II, and we have found a second-order transition experimentally, the ordered state must necessarily have the *"triple-*$\vec{q}$*" structure.*

The most general "triple-$\vec{q}$" structure is a superposition of the "single-$\vec{q}$" components in (1), i.e.,

$$\begin{aligned}
\vec{\mu}_A(\vec{r}) &= \textstyle\sum_k \vec{\mu}_A{}^k(\vec{r}), \quad \vec{\mu}_{A'}(\vec{r}) = \sum_k \vec{\mu}_{A'}{}^k(\vec{r}), \\
\vec{\mu}_B(\vec{r}) &= \textstyle\sum_k \vec{\mu}_B{}^k(\vec{r}), \quad \vec{\mu}_C(\vec{r}) = \sum_k \vec{\mu}_C{}^k(\vec{r}),
\end{aligned} \tag{3}$$

which only depend on α_k through $\alpha = \sum_k \alpha_k$. α can-

not be determined directly from a scattering experiment, but the sixth-order term in F fixes α to either 0° or 90°. To visualize the structure, we have plotted the basal-plane components of the A-site spins [Fig. 3(a)]. The spins are seen to form an incommensurable hexagonal lattice on top of the original nuclear lattice.

The magnetic neutron diffraction cross sections from a pair of satellites at $\vec{\tau} \pm \vec{q}_k$ are identical for the "single-$\vec{q}$" and the "triple-$\vec{q}$" structures. For the "single-$\vec{q}$" structure, the satellites reflect the contribution from a single magnetic domain characterized by $\vec{q}_k$, while for the "triple-$\vec{q}$" structure the satellites reflect the contribution from the $\vec{q}_k$ component of the moments. Thus the following question arises: Is it possible to distinguish *experimentally* between the "single-$\vec{q}$" and the "triple-$\vec{q}$" structures? The solution lies in considering the coupling to the lattice. The spin-lattice coupling is represented by additional terms in the free-energy expansion:

$$F_{SL} = iA[\psi(\vec{q}_1)\psi(\vec{q}_2)u(\vec{q}_3) - \psi(-\vec{q}_1)\psi(-\vec{q}_2)u(-\vec{q}_3) + \text{cyclic permutations}] + B\sum_k\{[\psi(\vec{q}_k)]^2 u(-2\vec{q}_k) + \text{complex conjugate}\}, \quad (4)$$

where $u(\vec{q}_k)$ is a periodic lattice distortion transforming under C_{2v} as A_1. The last term induces the usual magnetostriction with wave vector $2\vec{q}_k$. The first term induces lattice distortions that are 90° out of phase with the magnetization, with periodicities given by $\vec{q}_1$, $\vec{q}_2$, and $\vec{q}_3$. The lattice distortions are plotted in Fig. 3(b). Apart from the phase, the lattice distortions are identical in form with (3). The distortion is very similar to the distortion observed in the layered compounds $1T$-$TaSe_2$ and $2H$-$TaSe_2$[7] and gives rise to satellites in the neutron diffraction spectrum which generally coincide with the magnetic satellites. However, while the magnetic satellites $\{h \pm q, 0, 0\}$ vanish because of symmetry, the corresponding structural satellites are allowed. Since the coupling involves *two* different components, $\psi(\vec{q}_1)$ and $\psi(\vec{q}_2)$ of the order parameter, it is active only in the "triple-$\vec{q}$" state. *The existence of* $\{h \pm q, 0, 0\}$ *satellites is thus direct evidence of the "triple-*$\vec{q}$*" structure.* As the lattice distortion couples to second order in the primary order parameter, its temperature dependence in the critical region should be

$$|u(\vec{q}_k)| \propto (T_N - T)^{2\beta}, \quad (5)$$

in contrast to that of the primary order parameter

$$|\psi(\vec{q}_k)| \propto (T_N - T)^{\beta}. \quad (6)$$

In order to test (5), we compared the measured temperature dependences of the structural satellite $(1-q, 0, 0)$ and the magnetic satellite $(q, 0, 3)$ (Fig. 1). The Néel temperature was estimated to be 19.9 ± 0.1 K both from the peak in the elastic scattering away from the $(q, 0, 3)$ Bragg point and from the divergence in the width of the satellites close to T_N. The critical scattering, which was subtracted from the elastic scattering below T_N,

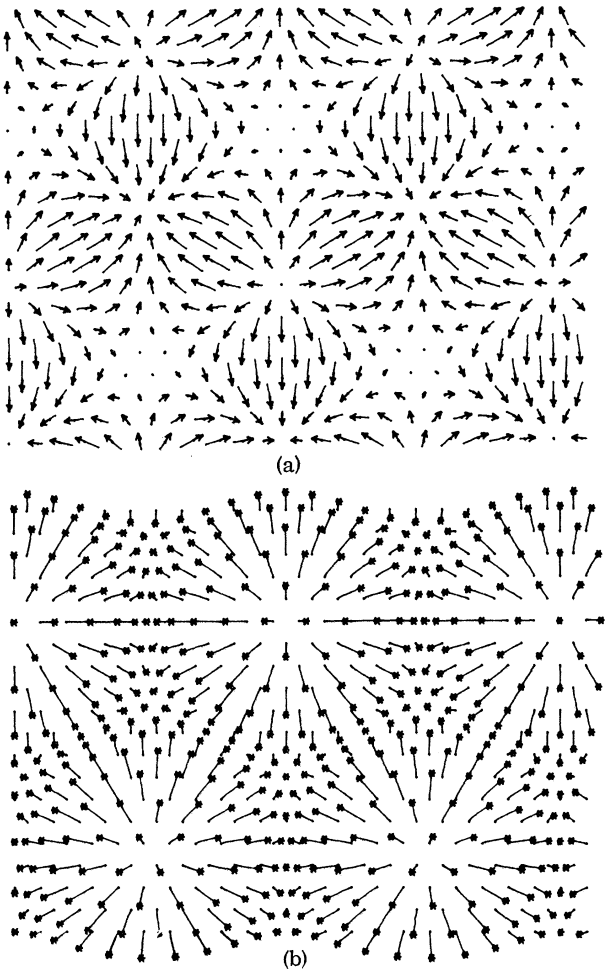

FIG. 3. The magnetic structure of neodymium for $\alpha = 0°$. (a) The basal-plane components (↑) of the spins in the A layers centered at the atomic positions of the undistorted lattice. (b) The accompanying lattice distortion (as indicated by lines with an asterisk at one end). The atoms are shifted to the positions of the * in the distorted lattice. For $\alpha = 90°$, (a) and (b) should in principle be interchanged.

was estimated from the elastic scattering above T_N by fits to (6) followed by estimates of the critical scattering using the scaling laws. After a few iterations, β converged at $\beta = 0.36 \pm 0.02$, in agreement with the theoretical value of $\beta \sim 0.38$ calculated to second order in ϵ.[4] The $(1-q, 0, 0)$ intensity is consistent with (5) $(2\beta = 1 \pm 0.3)$, but inconsistent with (6), thus confirming that the peak arises from a second-order coupling to the order parameter that only exists for the "triple-$\vec{q}$" structure. The possibility of multiple-scattering effects involving two magnetic satellites was ruled out by experimental tests and calculation.

The four parameters giving the magnitude and phase of the spins in the different layers, and the four parameters giving the corresponding lattice distortions still remain to be determined. Although intensities of approximately forty independent satellites are available this is a considerable numerical problem. Preliminary attempts indicate that $\mu_c \sim \mu_z \sim (10\text{–}20)\%$ of μ_h with $\theta \sim 180°$, and that the basal-plane lattice distortions are of the order of a few percent. The numerical problem may be somewhat reduced by deducing the ratio between the magnetic and the nonmagnetic contribution to each satellite from polarized-neutron data. A very interesting experiment would be to measure directly the lattice distortion by means of x-ray scattering.

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Effect of Refraction of *p*-Polarized Light on Angle-Resolved Photoemission from Surface States on Metals

A. Bagchi and N. Kar
Department of Physics and Astronomy and Center for Theoretical Physics, University of Maryland, College Park, Maryland 20742

and

R. G. Barrera
Institute of Physics, University of Mexico, Mexico City 20, Distrito Federal, Mexico

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It is suggested that the suppression of normal photoemission from surface states on a W(100) surface near the plasma frequency is due to refraction effects. Two model calculations are presented which are expected to bracket the real situation, and they both exhibit this property. Possible additional effects of refraction on the photoemission cross section are discussed.

It was reported in two recent Letters[1,2] that the angle-resolved photoemission in the direction of the surface normal from the surface state(s) of W(100) is strongly suppressed in intensity when the light frequency is close to the plasma frequency of tungsten. We show in this Letter, with the help of two separate model calculations, that the experimental observation can be explained in a simple and natural way when one takes into account the refraction of *p*-polarized light at the metal surface. To our knowledge, this is the first time that the importance of the electric field distribution in the surface region has been recognized in computing the matrix element for

