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Sublattice susceptibilities of neodymium metal

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The magnetic sublattice susceptibilities of atoms on the cubic and hexagonal sites of metallic Nd have been deduced from polarized-neutron-diffraction experiments over the temperature range from 1.7 to 100 K. Above 40 K both sites have the same susceptibility. Below the Néel point of 19.9 K the cubic site has a much larger susceptibility. Both susceptibilities have a cusp at the Néel point and a broad maximum near 8.5 K. The maximum covers the temperature region where anomalies have been reported in the specific-heat and neutron-diffraction data. These results are consistent with proposed models of the magnetic structure. The average of the two susceptibilities is in fair agreement with bulk susceptibility measurements.

INTRODUCTION

To develop more complete information on the very complex magnetic behavior of Nd, we have used the polarized-neutron technique to measure the magnetic susceptibilities of Nd ions on different crystallographic sites as a function of temperature. Nd has the double-hexagonal close-packed structure with a stacking sequence along the *c* axis of *ABAC*. The *A* layers (cubic sites) have nearest-neighbor coordination like that of the fcc structure and the *B* and *C* layers (hexagonal sites) have nearest-neighbor coordination like that of the hcp structure. Polarized-neutron-diffraction measurements on several Bragg peaks allow the determination of the separate moments induced by an applied field on the cubic and hexagonal sites, in contrast to a conventional bulk susceptibility experiment where the average moment is determined. From our knowledge of the magnetic structures of Nd it was expected that the magnetic susceptibilities of the cubic and hexagonal sites would be quite different below 20 K. This expectation has been confirmed.

The complete details of the magnetic structures of Nd are still uncertain, but some of the major features are well established.[1] There is a continuous transition at 19.9 K to a sinusoidally modulated structure with propagation vectors along [100] directions. The dominant magnetic component in this structure is on the hexagonal sites and oriented along the propagation vector. Much smaller components appear on the cubic sites. Below 8 K the structure becomes more complex with at least three sets of propagation vectors of different magnitudes. One of these propagation vectors has been associated with a modulated moment structure in which the dominant component is on the cubic sites.[2] Heat-capacity measurements by Forgan *et al.*[3] suggest that there are four magnetic transitions between 5 and 9 K.

EXPERIMENTAL DETAILS

The neutron measurements were performed at the HB-1 polarized-beam spectrometer at the High Flux Isotope Reactor. The single-crystal sample was approximately cubic in shape, 4 mm along an edge, and weighed 0.469 g. The sample was mounted with a [$\bar{1}$20] reciprocal-lattice vector (crystallographic *a* direction) vertical, parallel to the applied magnetic field. The temperature was varied between 1.7 and 100 K. The neutron wavelength was 1.067 Å and a Pu filter was used to remove the $\lambda/2$ contaminant.

The experiment consists of measuring the ratio of Bragg intensities when the neutrons are polarized parallel and antiparallel to the applied field. This intensity ratio is given by

$$R_i = [(1+\gamma_i)/(1-\gamma_i)]^2 , \tag{1}$$

where γ is the ratio of the magnetic to nuclear structure factors and the index i stands for a set of (hkl) indices. At each temperature we measured a group of $(10l)$ reflections where $l=0$, 1, 3, 4, 5, and 7. For $l=0,4$,

$$\gamma_l = 0.5 r_0 \gamma_N f_l (2\mu_c - \mu_h)/b \ , \tag{2}$$

and for $l=1,3,5,7$,

$$\gamma_l = 0.5 r_0 \gamma_N f_l \mu_h / b \ , \tag{3}$$

where r_0 is the classical electron radius, γ_N is the magnitude of the neutron moment expressed in nuclear magnetons, f_l is the magnetic form factor of Nd for the $(10l)$ reflection, μ_c and μ_h are the average moments (in Bohr magnetons) induced by the applied field on the cubic and hexagonal sites, and b is the nuclear scattering amplitude of Nd. We have restricted our measurements to rather low-angle reflections where the dipole approximation to the form factor should be accurate and have used the calculated dipole form factor of Stassis *et al.*[4] For the nuclear amplitude we have used $b=0.78\times10^{-12}$ cm.[5]

In a preliminary experiment we measured the intensity ratio (R_i) of several peaks as a function of applied field to make sure that we would be operating in a linear-response region. At 4.3 K, linear behavior was observed up to an applied field of at least 0.37 T. In the final experiment, we used a field of 0.243 T at temperatures up to 31.6 K, then increased the field to 0.486 T for temperatures up to 100 K, and finally used 0.728 T at 100 K. The observed intensity ratios were corrected for imperfect beam polarization, imperfect flipping efficiency, dead time in the counting system, and extinction. The extinction corrections were based on measurements of the flipping ratio as a function of wavelength for the strong peaks (004), (008) $(\gamma_l \sim 2\mu_c + 2\mu_h)$, and (102) $(\gamma_l \sim 2\mu_c + \mu_h)$. The reflections used in the susceptibility measurements were chosen to be those with small structure factors so that the extinction correction would also be small. The total of all the corrections corresponded to a change in γ of less than 7%.

After correcting the intensity ratios, the induced moments were calculated using Eqs. (1)–(3). The agreement among moment values determined from different Bragg peaks was reasonably good, as shown for a few temperatures in Table I. The μ_h values obtained from the (103) and (107) peaks were slightly higher than those obtained from the (101) and (105) peaks for temperatures below 20 K. This difference is beyond the bounds of the statistical errors indicated in Table I and indicates some systematic effect not considered in our data-reduction procedure. As possible causes of this behavior we have considered a more complex form factor and stacking faults, but we have no convincing argument to support either of these possibilities. Because the differences are fairly small we have used weighted means in the final analysis, and have assigned errors determined by deviations from these means.

In calculating the susceptibilities we have used for the internal field

$$H_i = H_0 - 4\pi D M \ , \tag{4}$$

where H_0 is the applied field, D is the demagnetizing factor, and M is the magnetization. M may be calculated from the average moment determined in the neutron experiments and we have used the spherical approximation of $\frac{1}{3}$ for D. We obtain

$$H_i = H_0 - 0.115\bar{\mu} \ , \tag{5}$$

where the fields are in T and $\bar{\mu}$ is in Bohr magnetons. The maximum demagnetization correction was about 5%.

RESULTS

The susceptibilities for the two sites are given in Fig. 1. Above 40 K the susceptibilities on both sites are identical, indicating that differences in crystal field and exchange effects are small compared to this temperature. As the Néel point is approached, the two susceptibilities begin to diverge with the cubic susceptibility being larger. Both show a cusp at 21 K, indicating that both sites are partially ordered below this temperature in agreement with the structure model proposed for Nd.[6] We believe these cusps appear at a temperature slightly above the Néel point because of the applied field. Below the magnetic ordering temperature, the susceptibilities at both sites rise to maxima at 8.5 K; the cubic-site

TABLE I. Moments in Bohr magnetons at selected temperatures in an applied field of 0.243 T.

Temp. (K)	$2\mu_c-\mu_h$ (100)	(104)	μ_h (101)	(105)	(103)	(107)
4.33	0.131(1)	0.129(2)	0.035(1)	0.035(1)	0.037(1)	0.039(2)
9.23	0.239(1)	0.232(1)	0.055(1)	0.055(1)	0.060(1)	0.061(1)
19.07	0.070(1)	0.070(1)	0.040(1)	0.039(1)	0.042(1)	0.042(1)
28.05	0.034(1)	0.033(2)	0.029(1)	0.029(1)	0.028(1)	0.032(2)

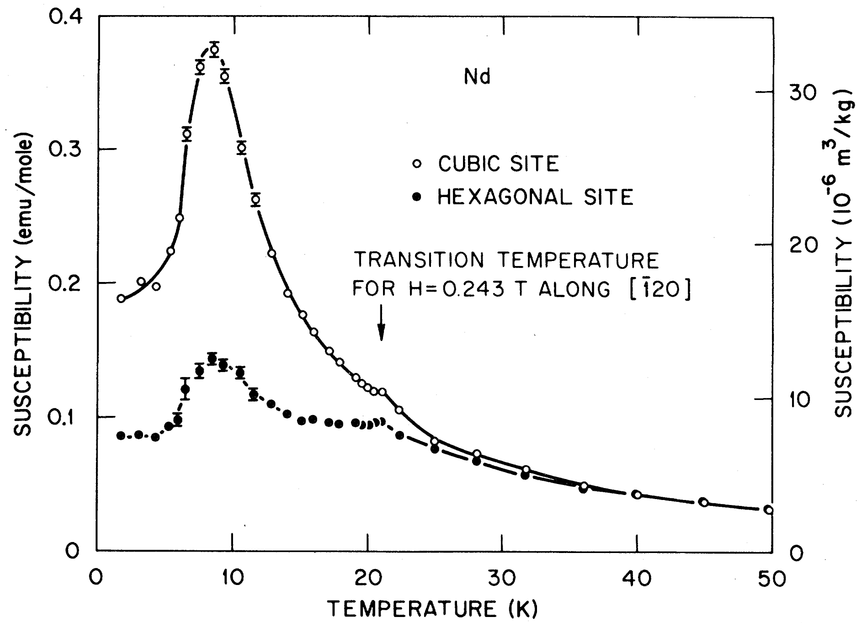

FIG. 1. Cubic and hexagonal susceptibilities as a function of temperature. Errors are equal to or less than the size of the data points except where indicated. The solid lines are guides to the eye. (For Nd, 1 emu/mole = 87.121×10^{-6} m^3/kg or 1 emu/mole = $1.791\mu_B$/T.)

susceptibility maximum being about 2.7 times higher than the hexagonal-site susceptibility. Between 8.5 and 5 K both susceptibilities decrease by the same fractional amount, and below 5 K the susceptibility at the cubic sites is about twice that at the hexagonal sites. Between the Néel point and 7.5 K, the temperature dependence of the susceptibilities is consistent with the proposed zero-field models which place the largest ordered component on the hexagonal sites. If this is true, the cubic sites should show the largest susceptibility because the cubic moments have greater freedom to respond to an external field. Below 7.5 K (at zero field) the magnetic structure changes with the major quantitative change being a much larger ordered component on the cubic sites accompanied by directional changes of the modulation vector describing the order on the hexagonal sites.[7] We believe that the broad maxima observed in the susceptibility data are connected with the multiple transitions in the temperature range from 5 to 9 K, as seen in the specific-heat data.[3]

The average of the cubic and hexagonal susceptibilities should be equal to the bulk susceptibility. We have measured the bulk susceptibility of the same sample using a vibrating-sample magnetometer which had been calibrated against a nickel sphere[8] and a superconducting niobium sphere. The two calibrations differed by only 2%. The susceptibilities were determined from the initial slope of induced moment versus field plots, varying the field from 0 to 0.2 T applied in the same direction as in the neutron experiment. Approximate demagnetizing corrections, similar to those used in the neutron case, were applied to the data. Above 9 K the induced moment was a linear function of the field. A small remanent moment and a slight nonlinearity were observed below 9 K. At 4.8 K the remanent moment was $3.7\times10^{-3}\mu_B$ per atom compared to an average induced moment of $0.295\mu_B$/T per atom. The remanent moment may be related to stacking faults because ferromagnetism has been observed in the metastable fcc phase of Nd.[9] The comparison between the average neutron susceptibility and the bulk susceptibility is shown in Fig. 2. Also shown are the bulk results of Johansson *et al.*[10] and of Behrendt, Legvold, and Spedding.[11]

Comparing first the neutron results with the bulk susceptibility of this work, we see that the bulk data differ by a few percent from the neutron data (see inset in Fig. 2). This may suggest an unknown systematic error in one or both of these experiments, or a real contribution to the bulk susceptibility which is not seen in the neutron experiment. If conduction-electron polarization were invoked to explain this difference it would have to be parallel to the total $4f$ angular momentum and antiparallel to the $4f$ spin, which is contrary to normal behavior in the rare-earth metals. Possible systematic errors which could combine to produce a constant fractional error of a few percent might originate in the calibration of the magnetometer, the field calibration of the supercon-

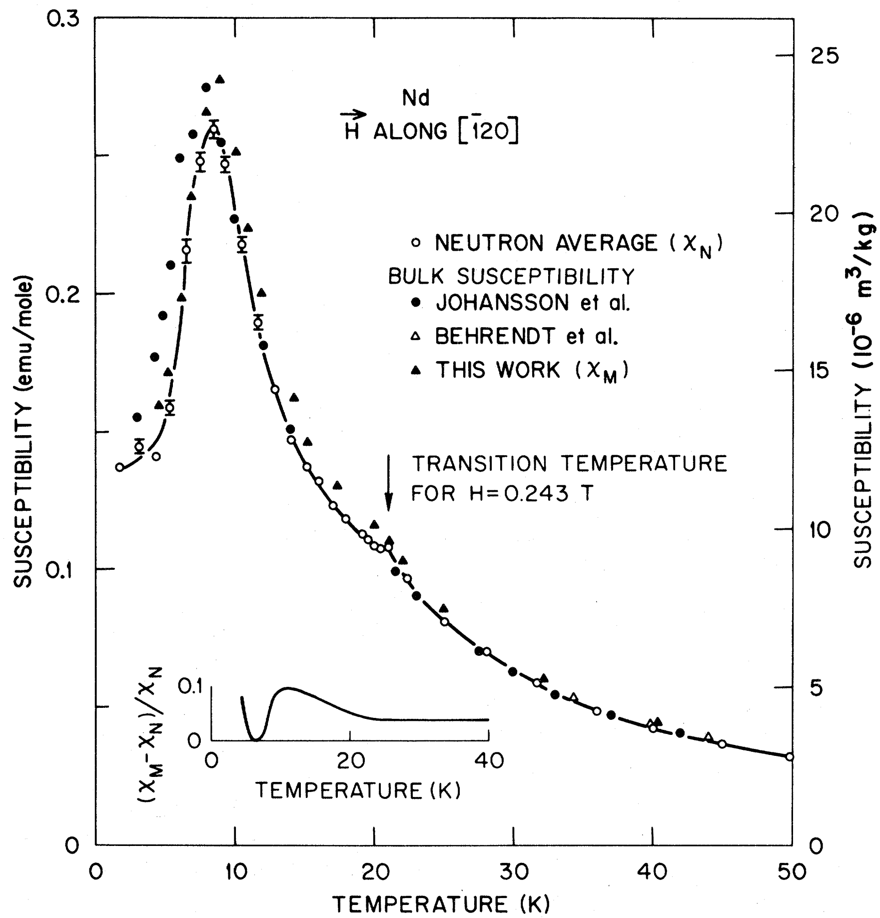

FIG. 2. Average susceptibility determined from the neutron measurements compared with various bulk susceptibility measurements. The solid line is a guide to the eye through the neutron results. The inset shows the fractional difference $(\chi_M-\chi_N)/\chi_N$ between the susceptibility determined from bulk data (χ_M) and polarized-neutron data (χ_N).

ducting magnet used in the neutron experiment, and the nuclear scattering amplitude used to normalize the neutron data. However, the variation of the fractional difference between the bulk and neutron susceptibilities is not constant. Indeed, in the temperature range from 6 to 12 K the variation (inset of Fig. 2) is suggestive of a slight shift (about 0.4 K) between the temperature scales for the two experiments. The possibility of such a shift is plausible because in neither experiment were the thermometers in direct contact with the sample and hence there would have been a temperature difference between the thermometer reading and the correct sample temperature in either experiment. For example, if the temperature scale of our bulk data is shifted down by 0.4 K there is a constant difference of about 4% between the bulk and the neutron data above 9 K. Below this temperature the fractional difference increases to about 11% at 4 K.

When comparing the neutron results and the bulk susceptibility of Johansson *et al.*[10] there is remarkable agreement above 9 K, whereas below 9 K the bulk data lie above neutron results. The data of Johansson *et al.* were obtained on a different sample and the weight of their sample was somewhat ambiguous due to oxidation of the surface.[12] This may account for the discrepancy between the two sets of bulk susceptibility data, and there may be problems with the relative temperature scales as discussed above. We believe that the bulk and the neutron susceptibilities are in reasonable agreement down to 9 K. Below this temperature the bulk susceptibility is higher than the susceptibility determined by neutron diffraction. At the present, we are unable to explain the latter observation.

In Fig. 3 is shown the inverse susceptibility, as determined by the neutron average, compared with the free-ion behavior. At the upper end of the tem-

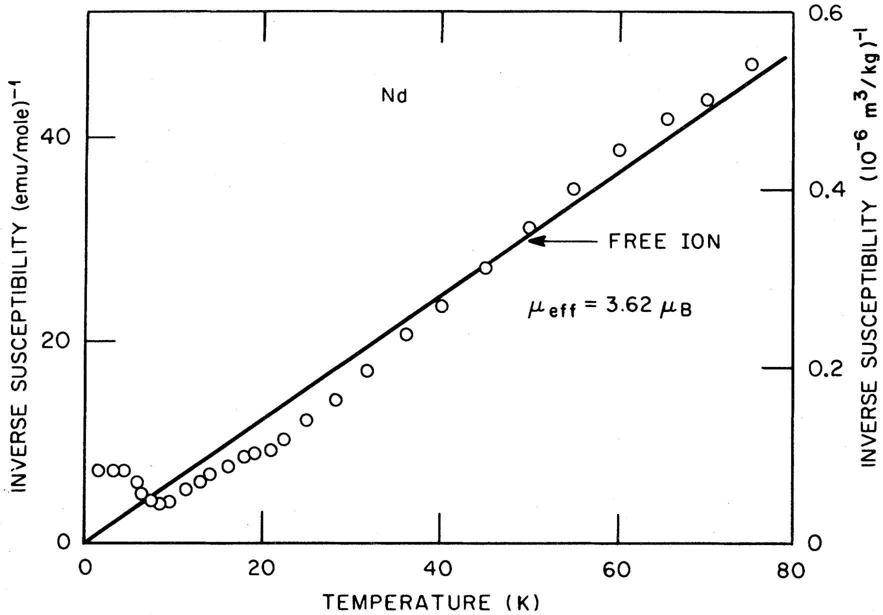

FIG. 3. Inverse average susceptibility from the neutron measurements compared with free-ion behavior.

perature range the experimental slope is close to the free-ion value which is characteristic of an effective moment of $3.62\mu_B$.

SUMMARY

Below the Néel point the cubic susceptibility is much larger than the hexagonal susceptibility. Both susceptibilities show cusps near the Néel point and broad maxima at the lower transition temperature near 8.5 K. The principal cause of the difference in susceptibility is the different exchange fields at the two sites produced by the magnetic structure. The susceptibilities are qualitatively consistent with proposed models of the magnetic structures.

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