CONF-731104-7

MAGNETICALLY INDUCED LATTICE DISTORTIONS IN THE NEPTUNIUM MONOPNICTIDES

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Prepared for:

19th Annual Conference on Magnetism and Magnetic Materials,
Boston, Massachusetts, November 13-16, 1973

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Argonne National Laboratory, Argonne, Illinois 60439

ABSTRACT

The lattice parameters of the neptunium monopnictides (NaCl crystal structure) have been measured between 5 and 300°K by X-ray diffraction. NpN becomes ferromagnetic at 87°K. At T_C a rhombohedral distortion, which indicates that the $\langle 111 \rangle$ is the easy axis, is observed. At 5°K, the rhombohedral angle is $60.46 \pm 0.02^\circ$. NpP exhibits a tetragonal distortion at 74°K, at which temperature the antiferromagnetic 3+, 3- structure becomes commensurate with the lattice. At 5°K $c/a = 0.9958 \pm 2$. NpAs becomes tetragonal at $T_N = 175^\circ\text{K}$ when the material has a 4+, 4- structure. However, NpAs returns to being a cubic at 142°K at which temperature the magnetic structure is the simple + - (type I) configuration. The 'return' to cubic is first order; the volume of the unit cell expands by 0.23%. NpSb, which orders antiferromagnetically at 207°K with the type I structure remains cubic in the ordered regime.

INTRODUCTION

The onset of magnetic order in a crystal lattice may lead to a reduction in symmetry of that lattice. For example, if a magnetic vector parallel to the [001] axis is introduced into a cubic lattice the symmetry is reduced from cubic to tetragonal. The ordering process is caused by exchange interactions, which are frequently anisotropic and depend on the interatomic distances. Another important interaction is electrostatic in nature, and occurs when neighboring atoms have aspherical electron-cloud distributions. This electrostatic interaction is especially important when the spin-orbit coupling is strong and L is a good quantum number. The magnetization density is then effectively tied to the direction of the magnetic moment. The magnetostriction of the rare-earth materials is primarily a consequence of this electrostatic interaction. From a macroscopic point of view, the energy of these interactions is frequently minimized if the lattice distorts at the ordering temperature. The magnetic and crystallographic symmetry are then compatible. Examples of this process are the transition-metal oxides¹ and the rare-earth monopnictides.² As part of a general study that includes magnetization, Mössbauer, resistivity, and neutron-diffraction measurements on the neptunium monopnictides,^{3,4} we have measured the lattice parameters of these compounds (NaCl structure) between 5 and 300°K.

*Performed under the auspices of the U.S. Atomic Energy Commission.

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EXPERIMENTAL

The sample preparation³ and experimental technique^{5,6} have been described previously. Polycrystalline samples have been used. We analyze the X-ray diffraction profiles with a least-squares process that fits a calculated X-ray profile to the experimental intensities. A simple Cauchy function is used to simulate the diffraction profiles.⁷

$$y_{ij} = \frac{m_{ij} L_p S}{\Delta} \left/ \left[1 + \left(\frac{2\theta_1 - 2\theta_j}{\Delta/2} \right)^2 \right] \right.$$

where y_{ij} is the intensity from a reflection hkl_j at the position $2\theta_j$, m_{ij} is the multiplicity of the reflection, L_p is the Lorentz-polarization factor, S is the scale factor, $2\theta_j$ is the calculated central position of the diffraction peak, and Δ is the full width at half maximum (FWHM) of the diffraction profile. At the position $2\theta_j$ the total intensity is $\sum y_{ij}$, where the sum is over all reflections and all incident wavelengths (i.e. the α_1 and α_2 components). The parameters S , Δ , and the constant background level are obtained by measuring the diffraction profiles above the ordering temperature. The FWHM is a function of the diffractometer and of the sample homogeneity and strain. In most cases, the FWHM does not vary when the lattice distorts. The least-squares process rapidly converges and gives an excellent fit ($\chi^2 \sim 1$) between the calculated and observed diffraction profiles. This analysis gives accurate values for the c/a ratio, which is the main interest in the experiment. To obtain absolute values of c and a we have used a computer program,⁸ which requires a series of diffraction peak positions as input.

NpN

Neptunium nitride becomes ferromagnetic at $T_C = 87^\circ\text{K}$. At the same temperature the unit cell distorts from cubic to rhombohedral. Above T_C a rhombohedral unit cell with an angle α of 60° may be used to describe the structure. The trigonal axis of this unit cell is the $\{111\}$ axis of the cubic unit cell. When the distortion at T_C occurs the $\{111\}$ axis is either compressed or stretched, the rhombohedral angle becoming greater than or less than 60° , respectively. A convenient description of this distortion is to define a length ' c ' as a distance along the unique trigonal axis and ' a ' as a distance in the plane perpendicular to ' c ' such that ' c/a ' = 1.00 in the cubic phase. This definition is especially useful in comparing the magnitude of trigonal and tetragonal distortions. The relationship between the change in the rhombohedral angle $\Delta\alpha$ and the ' c/a ' ratio is given by $\Delta\alpha = -8/\sqrt{27} (c-a)/a$ radians. In Fig. 1, we present the variation of these equivalent lattice parameters in the trigonal phase, as well as the variation of the cube edge in the paramagnetic phase.

The rhombohedral distortion in NpN indicates that the easy direction of the magnetic moments is either in the $\{111\}$ plane or

perpendicular to it. This information cannot be obtained from neutron-diffraction experiments on polycrystalline ferromagnets. At 5°K the value of $(c-a)/a = -52 \times 10^{-4}$ where c and a are defined above.

Fig. 1. Variation with temperature of the equivalent lattice parameters in NpN.

The variation with temperature of the lattice parameters of NpP have been reported.⁶ Briefly stated, NpP orders antiferromagnetically at 130°K. The (001) ferromagnetic sheets are stacked along the c axis with a sinusoidal variation of the moment from sheet to sheet.⁴ The repeat distance is 2.78 ± 0.08 unit cells. This magnetic structure has tetragonal symmetry, however, the cubic lattice parameter shows no discontinuity at T_N (see Fig. 2). At 74°K another transition occurs and the magnetic cell becomes commensurate with 3.0 chemical unit cells. At the same temperature, the X-ray experiments observe a large tetragonal distortion. At 5°K $c/a = 0.9958$, i.e. $(c-a)/a = -(42 \pm 2) \times 10^{-4}$.

Fig. 2. Variation with temperature of the lattice parameter of NpP.

NpP

NpAs

NpAs becomes antiferromagnetic at $T_N = 175^\circ\text{K}$. The high-temperature magnetic structure of NpAs is very similar to that described for NpP in that it consists of a stacking of ferromagnetic sheets in a $4+, 4-$ sequence along the c axis. A tetragonal distortion is observed by X-rays at T_N , as shown in Fig. 3. At 143°K $(c-a)/a = -(8 \pm 2) \times 10^{-4}$. Neutron experiments on NpAs at temperatures below $\sim 145^\circ\text{K}$ indicate that the magnetic structure is type I, in which the ferromagnetic sheets are

Fig. 3. Variation with temperature of the lattice parameter of NpAs.

the lattice parameter remains unchanged (see Fig. 3).

stacked in the simple + - sequence. The transition from the 4+, 4- to the + - sequence appears from the neutron experiments to be spread over several degrees, but in the X-ray experiments we observe a first-order transition in which the unit cell distorts from tetragonal (143°K) to cubic (142°K). We are unaware of any other material that transforms from tetragonal to cubic in the ordered regime. Not surprisingly, considerable strain is observed in the lattice just below 142°K, but the symmetry is clearly cubic $|(c-a)/a| \leq 3 \times 10^{-4}$. On further cooling,

NpSb

NpSb becomes antiferromagnetic at 207°K. The magnetic structure at all temperatures below T_N is the type I. Neptunium antimonide proved difficult to prepare and the X-ray diffraction profiles were very broad. The sample also contained a small amount of Np_3Sb_4 . Because of these difficulties precise lattice parameters could not be obtained. No evidence for a crystallographic distortion was found in NpSb. The limit of our sensitivity is such that $|(c-a)/a| \leq 15 \times 10^{-4}$ at 5°K.

Fig. 4. Temperature dependence of the volume of the unit cell (relative to 300°K) for the neptunium monopnictides.

DISCUSSION

The volume changes relative to room temperature are shown in Fig. 4 as a function of temperature for the four compounds. At high temperatures the straight-line behavior reflects the regular thermal expansion of the lattice and, as expected, this value increases with increasing lattice parameter. The coefficients of thermal expansion (5.5 for NpN, 9.6 for NpP, 10.3 for NpAs, and 17.0 for NpSb; all ± 1.0 and in units of $10^{-6}/K^\circ$) are comparable to those of the uranium monopnictides. At lower temperatures the volume contraction in NpN ($T_C = 87^\circ K$) and NpSb ($T_N = 207^\circ K$) appear normal, indicating that the transitions are not first order. Recall that NpN distorts rhombohedrally at T_C , but, within our experimental uncertainty, the volume of the unit cell varies smoothly through this transition. Similarly, second-order transitions occur at T_N in NpP ($130^\circ K$) and NpAs ($175^\circ K$). However, at lower temperatures both NpP and NpAs exhibit first-order transitions in which a discontinuity in the unit-cell volume is observed. These transitions are associated with changes in the magnetic structures. Large anomalies are also observed in the electrical resistivities of NpP and NpAs.⁹

In conclusion, the X-ray measurements provide a wealth of new and valuable information on the neptunium monopnictides. Indeed a complete understanding of these materials will clearly have to account for the crystallographic symmetry and the unexpected distortions that occur in the ordered state.

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