Structural and Magnetic Properties of the Intermetallic Compound $NpMn_2Ge_2$*

W. SCHÄFER**, G. WILL

Mineralogisches Institut, Universität Bonn, D-5300 Bonn, F.R.G.

F. J. LITTERST, W. POTZEL, G. M. KALVIUS

Physik Department E15, Technische Universität München, D-8046 Garching, F.R.G.

S. FREDO and J. GAL

Nuclear Engineering Department, Ben-Gurion University and Nuclear Research Center of the Negev, Beer Sheva, Israel

Among the intermetallic compounds of neptunium very few show localized 5f character. The large spatial distribution of the 5f electrons predicts their tendency to hybridize with nearest neighbours 5f and with p or d bands produced by ligand partners. Delocalization of the 5f electrons may lead in certain cases to a reduction of the ordered magnetic moments, to spin fluctuation phenomena and to changes of isomer shifts [1]. Isostructural intermetallic compounds NpM_2X_2 (M = Cr, Fe, Co, Ni, Cu; X = Si, Ge) are known to order magnetically at low temperatures [2]. It has been pointed out that crystal-field excitations and admixture of low lying crystal-field states play a major role in the magnetic properties of these series [3]. The compounds containing Mn, however, exhibit ordering temperatures close to room temperature. In the present contribution we report on the $NpMn_2Ge_2$ intermetallic compound which has been studied by means of neutron diffraction and Mössbauer effect.

Experimental

The $NpMn_2Ge_2$ ingot sample was prepared by arc-melting stoichiometric amounts of the metals in a dry argon atmosphere. X-ray diffraction measurements showed that a single phase was obtained. The samples were encapsulated in triple-sealed Al containers to prevent leakage of the Np.

The neutron diffraction measurements were performed on the powder diffractometer of Bonn University at the DIDO research reactor of the KFA Jülich. This diffractometer is equipped with a linear position-sensitive scintillation detector [4]. The neutron wavelength used was 1.09 Å. Diffraction patterns were recorded at temperatures between 340 and 16 K.

Mössbauer spectra of the 59.6 KeV ($5/2 \rightarrow 5/2$) nuclear transition in ^{237}Np were obtained by standard transmission geometry. The source used was ^{241}Am in the metal form.

Results

Crystal Structure

$NpMn_2Ge_2$ crystallizes in the tetragonal space group *I4/mmm* with two formula units per cell. The lattice parameters were refined by least-squares fits of profile analysed neutron peak positions at temperatures of 340, 300 and 16 K (Table I). The atoms occupy the following positions: Np in 2(a) (0, 0, 0); Mn in 4(d) $(0, \frac{1}{2}, \frac{1}{4})$; Ge in 4(e) $(0, 0, z)$ (Fig. 1). The z parameter of Ge was refined from the nuclear scattering intensities to $z = 0.386(1)$.

TABLE I. Lattice Parameters of $NpMn_2Ge_2$ for Various Temperatures due to Least-squares Refinement of Profile Analysed Neutron Reflection Positions

T (K)	a (Å)	c (Å)
340	4.016 ± 0.002	10.819 ± 0.009
300	4.011 ± 0.001	10.815 ± 0.007
16	4.000 ± 0.001	10.797 ± 0.005

Magnetic Structure

The identification of magnetic scattering contributions in the neutron diffraction patterns is based on intensity calculations for ferro- and antiferromagnetic moment configurations involving both the Np and the Mn sublattices. Due to the expected weak magnetic scattering contributions, the neutron diffractograms had to be analysed very carefully for intensity variations with temperature. This was done by individual peak profile analysis (Fig. 2). The most remarkable results are: distinct intensity enhancements of the 101, 004, 103 and 112 reflections and no additional superlattice peaks. The findings can be explained by the assumption of ferromagnetic ordering of both the Np and the Mn ions. Least-squares fits of the observed nuclear and magnetic intensities revealed the existence of ferromagnetic order already below 340 K. The magnetic moments obtained at 340, 300 and 16 K are 1.3(3) μ_B, 1.4(3) μ_B and 2.0(8) μ_B for the Np ion and 0.8(3) μ_B, 1.1(3) μ_B and 1.4(8) μ_B for the Mn ion, respectively. The refinement

*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

**Author to whom correspondence should be addressed at: Univ. Bonn in KFA Jülich MIN/ZFR, Postfach 1913, D-5170 Jülich, F.R.G.

0020-1693/87/$3.50

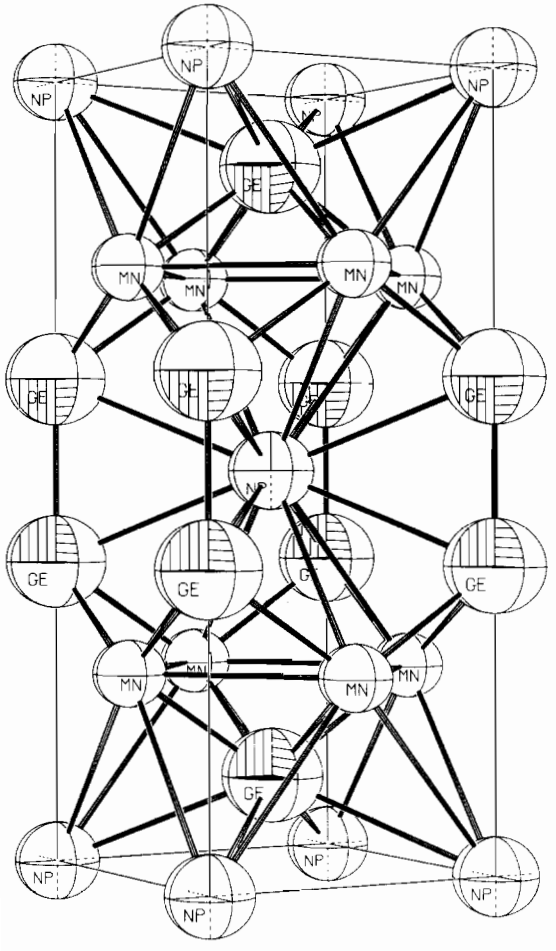

Fig. 1. Tetragonal crystallographic unit cell of $NpMn_2Ge_2$.

calculations were performed with 20 peaks containing 39 *hkl* reflections using the program POWLS [5]. The R values obtained were 5.3%, 5.2% and 12.4% for the 340, 300 and 16 K data, respectively. The discrepancies between observed and calculated intensities for the 16 K data are not yet explained. We observe a rather pronounced decrease of intensity mainly at the 001 reflections (e.g. 002, 006 and 008) when going from 300 to 16 K. This effect may be attributed to reorientation of certain crystal planes during the cooling procedure.

Mössbauer Effect Results

The Mössbauer effect studies of $NpMn_2Ge_2$ were performed up to room temperature. They yield well-resolved magnetic hyperfine patterns (Fig. 3). This indicates that T_C must be above room temperature. The magnetic hyperfine field B_{eff} at saturation is 290 T, which corresponds to $\mu_{ord} = 1.3(2)\,\mu_B$ [6].

Discussion and Conclusions

It has recently been reported that the isostructural UMn_2Si_2 and UMn_2Ge_2 order ferromagnetically below 380 K [7]. In these cases a temperature-dependent ordered moment of maximum 3 μ_B on the Mn ion is claimed. Above 100 K, at the U site, however, no ordered moment is observed. We thus conclude that the magnetic order is driven by the Mn atoms.

The fact that we observe in $NpMn_2Ge_2$ the same ordering temperature for both the Np and the Mn

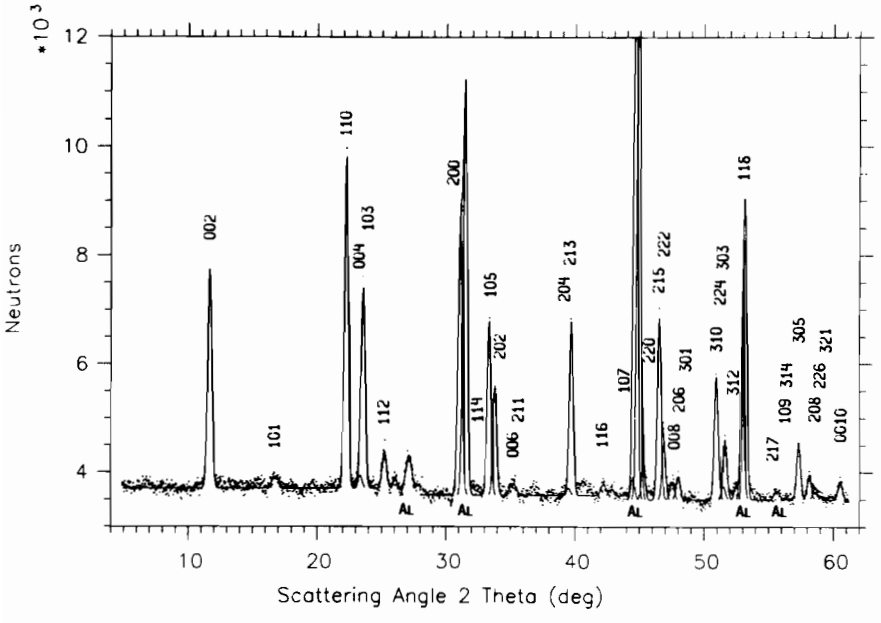

Fig. 2. Profile analysed neutron diffraction pattern of $NpMn_2Ge_2$ at T = 300 K.

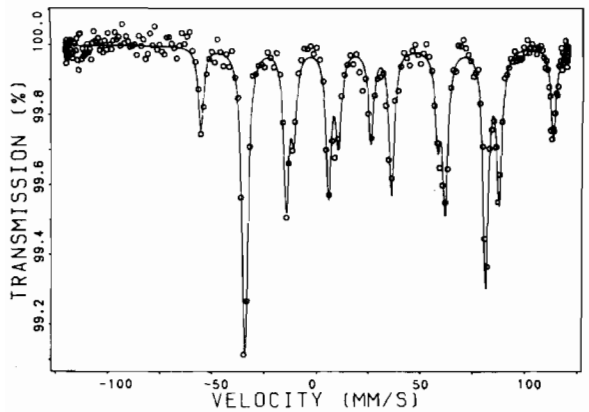

Fig. 3. Mössbauer spectrum of ^{237}Np in $NpMn_2Ge_2$ at T = 4.2 K.

sites with nearly saturated magnetic moments up to room temperature, clearly indicates strong exchange interaction between the Mn and the Np moments. The isomeric shift (+9.5 mm/s) is compatible with a Np^{3+} (I_4 ground state) ion. In the tetragonal symmetry the $\Gamma_5{}^t$ doublet is split by exchange. This doublet possesses a moment of 1.5 μ_B which is in agreement with the Mössbauer data and the high temperature neutron results. The moment derived from the neutron data at low temperature is somewhat higher and for the moment this discrepancy is not understood.

Acknowledgements

This work has been funded by the German Federal Minister for Research and Technology (BMFT) under contract numbers 03-WI1BON, 03-GA1BEE and 0.3-KA1TUM and the National Council for Research and Development (NCRD), Israel.

References

1 J. Moser, J. Gal, W. Potzel, G. Wortmann, G. M. Kalvius, B. D. Dunlap, D. J. Lam and J. C. Spirlet, *Physica B, 102,* 199 (1980).
2 A. J. Freeman and G. H. Lander, 'Handbook on the Physics and Chemistry of the Actinides', North Holland, Amsterdam, 1985, p. 156.
3 G. M. Kalvius, W. Potzel, J. Moser, F. J. Litterst, L. Asch, J. Zankert, U. Potzel, A. Kratzer, M. Wunsch, J. Gal, S. Fredo, D. Dayan, M. P. Dariel, M. Boge, J. Chappert, J. C. Spirlet, U. Benedict and B. D. Dunlap, *Physica B, 130,* 393 (1985).
4 W. Schäfer, E. Jansen, F. Elf and G. Will, *J. Appl. Crystallogr., 17,* 159 (1984).
5 G. Will, E. Jansen and W. Schäfer, 'POWLS-80', program for calculation and refinement of powder diffraction data, *Report Jül-1867,* KFA Jülich, 1983.
6 G. H. Lander and B. D. Dunlap, *Phys. Rev. Lett., 33,* 1046 (1974).
7 A. Szytula, S. Siek, J. Leciejewicz, A. Zygmunt and Z. Ban, *Dix-septièmes Journées des Actinides,* Lausanne, Switzerland, 1987.