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Journal of Alloys and Compounds 323–324 (2001) 516–519

Journal of ALLOYS AND COMPOUNDS

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Structural and magnetic properties of RFe_4P_{12} (R=Pr, Nd) studied by neutron diffraction

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Abstract

In this work we present a neutron powder diffraction study of the ternary rare-earth phosphides $PrFe_4P_{12}$ and $NdFe_4P_{12}$. High-resolution measurements of the structural temperature dependence reveal large-amplitude thermal vibrations of the rare-earth ions, consistent with speculations that the ion is weakly bound in an oversized atomic 'cage' formed in the skutterudite crystal structure. In addition, low temperature neutron diffraction measurements of RFe_4P_{12} (R=Pr, Nd) were performed. Whereas the proposed long-range antiferromagnetic ordering in $PrFe_4P_{12}$ could not be confirmed, $NdFe_4P_{12}$ orders ferromagnetically below $T_C=1.94$ K with an ordered magnetic Nd^{3+} moment of 1.61(7) μ_B at 1.5 K. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: A. magnetically ordered materials; C. neutron diffraction; D. phase transitions; E. neutron scattering, diffraction

1. Introduction

The ternary rare-earth (R) phosphides with general formula RT_4P_{12} (R=La, Ce, Pr, Nd, Sm, and Eu; T=Fe, Ru, and Os) have been reported to crystallize in a bcc crystallographic structure [1]. This structure is derived from the $CoAs_3$- and WAl_{12}-type structures by filling the icosahedral and octahedral voids with R and T atoms, respectively [1], and is also known as the filled skutterudite structure. The rare-earth iron phosphates RFe_4P_{12} have been investigated by numerous macroscopic methods such as measurements of the electrical resistivity, magnetization, specific heat, and thermoelectric power. Various exciting physical properties were found for this class of compounds that can be associated with magnetic ordering or f-electron hybridization. Among the most striking features of these compounds is the occurrence of superconductivity in $LaFe_4P_{12}$ [2] with a superconducting transition temperature T_C of 4.08 K. $LaFe_4P_{12}$ is one of only few Fe compounds to exhibit superconductivity. Mössbauer effect measurements [3] revealed a very small upper limit of 0.01 μ_B for the magnetic moment of Fe ions in $LaFe_4P_{12}$, which is consistent with the occurrence of superconductivity, in spite of the large Fe concentration of ~24 at.%.

Measurements of the electrical resistivity of $CeFe_4P_{12}$ [4] exhibit non-metallic, insulating behavior, whereas, e.g. $PrFe_4P_{12}$ and $NdFe_4P_{12}$ are metals. Further investigations of the Pr- and Nd-compounds included measurements of the specific heat [5,6], magnetization [5] and electrical resistivity [5,7]. The results of these macroscopic measurements were consistent with ferromagnetism for $NdFe_4P_{12}$ below 2.0 K and antiferromagnetism for $PrFe_4P_{12}$ below 6.2 K, even though the magnetic structure of the ground state remained not clear. On the other hand it has been speculated about a non-magnetic crystalline electric field ground state in $PrFe_4P_{12}$ which would be inconsistent with the proposed antiferromagnetic ordering with a rather moderate critical temperature. In addition, measurements of the thermoelectric power [7] implied some anomalous nature of electron hybridization and found evidence for Kondo scattering in $PrFe_4P_{12}$.

In this work we report on new investigations of the magnetic ground state of $PrFe_4P_{12}$ and $NdFe_4P_{12}$ using neutron diffraction which is the method of choice for investigating magnetic ordering and which, as a microscopic method, is complementary to the macroscopic methods used in previous reports.

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0925-8388/01/$ – see front matter
PII: S0925-8388(01)01163-X

2. Experimental details

Polycrystalline powder samples of $PrFe_4P_{12}$ and $NdFe_4P_{12}$ were synthesized by the Sn flux method as described in Ref. [5]. The neutron diffraction experiments were performed at the spallation neutron source SINQ of the Paul Scherrer Institute in Villigen, Switzerland. The chemical structure and its temperature dependence was measured on the new high resolution powder diffractometer HRPT, using a vertically focusing Ge monochromator and the neutron wavelength 1.886 Å, monochromator reflection Ge(133), and 1.372 Å, Ge(711), respectively. The magnetic structures were investigated on the cold neutron powder diffractometer DMC with a vertically focusing graphite monochromator C(002) and the wavelength 3.801 Å. In order to remove higher-order neutron wavelengths a graphite filter was placed between the monochromator and the sample. On both instruments radial collimators between sample and detectors suppress Bragg peaks from the sample environments. For the measurements down to 15 K (HRPT) a closed cycle He refrigerator was used, whereas temperatures down to 1.5 K (DMC) were reached with a He cryostat. The refinements of the powder diffraction patterns were done using the Rietveld method and the program FULLPROF [8].

3. Results and discussion

3.1. The chemical structure and its temperature dependence

The room temperature neutron powder diffraction patterns of $PrFe_4P_{12}$ and $NdFe_4P_{12}$ are shown in Figs. 1 and 2, showing the observed, calculated and difference patterns. The Nd-compound showed an impurity phase of a few percent which could not be identified. The additional peaks are well separated from the peaks due to the main phase ($NdFe_4P_{12}$) and could be excluded for the structural and magnetic refinements. The fit of the data confirmed the filled skutterudite structure of the compounds. $PrFe_4P_{12}$ and $NdFe_4P_{12}$ crystallize in the cubic space group *Im3* (No. 204) with two formula units per unit cell. The lattice parameters at room temperature are 7.8126(1) and 7.8087(2) Å for the Pr- and Nd- compound, respectively. The resulting crystallographic data for both compounds are summarized in Table 1. Note the large value of the Debye–Waller parameters *B* for the rare-earth ions which is considerably larger than the ones for Fe and P. In order to investigate this point and to investigate the thermal behavior of the skutterudite structure in these compounds, $PrFe_4P_{12}$ was measured at several temperatures between 15 K and room temperature. Fig. 3 shows the temperature dependence of the lattice parameter *a* as well as the temperature dependence of the *B* parameters for Pr, Fe, and P. The thermal contraction of the unit cell as well as the decrease of thermal vibrations with decreasing temperatures, which reduces the Debye–Waller factor, is nicely demonstrated and shows a regular behavior. Nevertheless over the whole temperature range the Debye–Waller factor of Pr stays dramatically enhanced as compared to the values for the other elements in the compound. This unusual behavior is clear evidence for large-amplitude thermal ‘rattling’ of the Pr ion in $PrFe_4P_{12}$, a mechanism thought to be responsible for the generally low thermal conductivities found among filled skutterudites. A similar

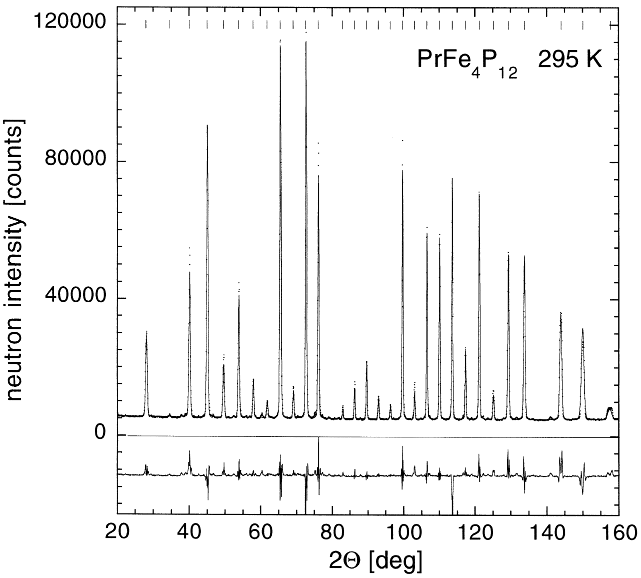

Fig. 1. Observed, calculated and difference neutron diffraction patterns of $PrFe_4P_{12}$ at room temperature. The vertical bars at the top indicate Bragg peak positions.

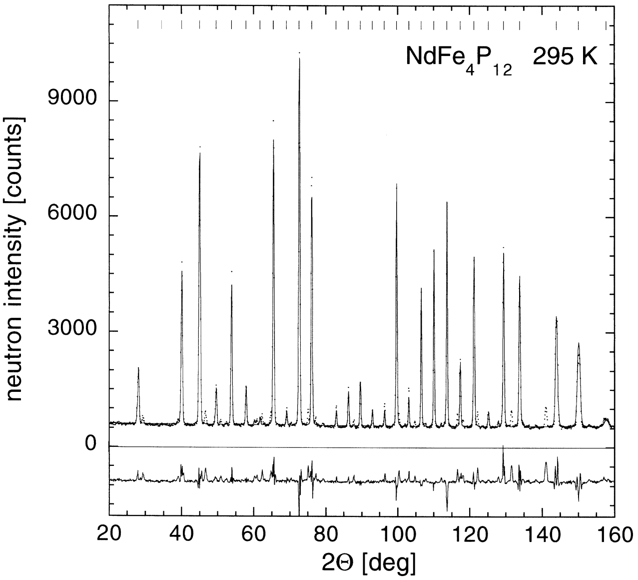

Fig. 2. Observed, calculated and difference neutron diffraction patterns of $NdFe_4P_{12}$ at room temperature. The vertical bars at the top indicate Bragg peak positions.

Table 1
The structural data of $PrFe_4P_{12}$ and $NdFe_4P_{12}$ at $T=295$ K, derived by neutron powder diffraction; *a*, lattice constant; (*x*, *y*, *z*), atomic coordinates; *B*, Debye–Waller factor

$Im\bar{3}$	$PrFe_4P_{12}$	$NdFe_4P_{12}$
a (Å)	7.8126(1)	7.8087(2)
R (*x*, *y*, *z*), R=Pr, Nd	0, 0, 0	0, 0, 0
Fe (*x*, *y*, *z*)	1/4, 1/4, 1/4	1/4, 1/4, 1/4
P (*x*, *y*, *z*)	0, 0.3521(2), 0.1508(2)	0, 0.3535(6), 0.1519(5)
B(R) ($Å^2$), R=Pr, Nd	0.40(8)	0.25(9)
B(Fe) ($Å^2$)	0.12(2)	0.10(2)
B(P) ($Å^2$)	0.20(2)	0.18(3)

behavior of thermal parameters has also been reported for the isostructural compound $YbFe_4Sb_{12}$ [9]. Static disorder at the Pr site, e.g. incomplete fillings, will also result in a large *B* parameter. Therefore we have repeated the refinements of each data set allowing the Pr occupation parameter to vary in the Rietveld analysis. No significant deviation from stoichiometric composition was found. Therefore it can be concluded that our high resolution neutron diffraction investigation reveals large-amplitude thermal vibrations of the Pr ions, consistent with speculations that the rare-earth ion is weakly bound in an oversized atomic 'cage' formed in the skutterudite crystal structure.

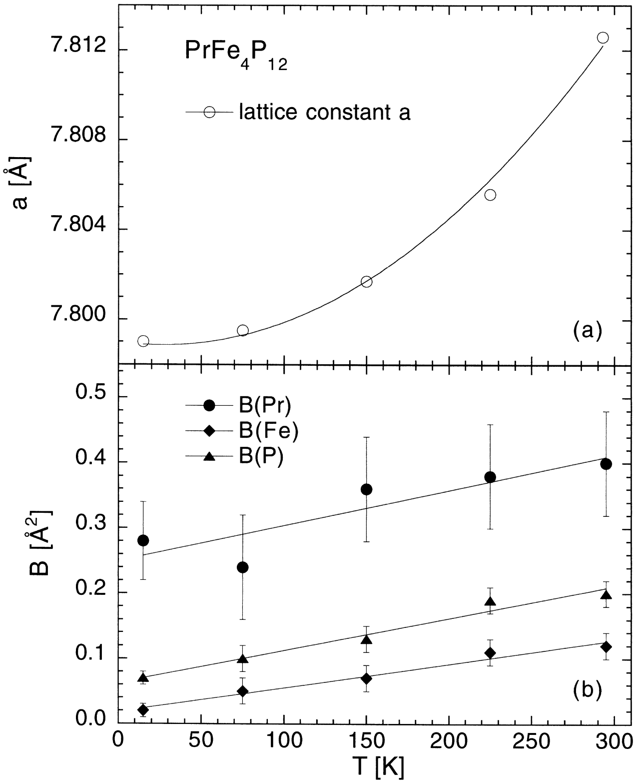

Fig. 3. (a) Temperature dependence of the lattice constant of $PrFe_4P_{12}$. A quadratic fit of the data is used as guide to the eye. (b) Temperature variation of the Debye–Waller factors *B* in $PrFe_4P_{12}$ for Pr, Fe and P, respectively. The lines are linear least-squares fits of the data.

3.2. Low-temperature neutron diffraction data

A part of the DMC low temperature neutron powder diffraction data for $NdFe_4P_{12}$ is shown in Fig. 4, at temperatures above and below the proposed Curie temperature $T_C=1.94$ K. T_C was derived by specific heat measurements (Y. Aoki, T.D. Matsuda, H. Sugawara and H. Sato, unpublished results) of a sample synthesized in a similar way as the one used in the neutron diffraction

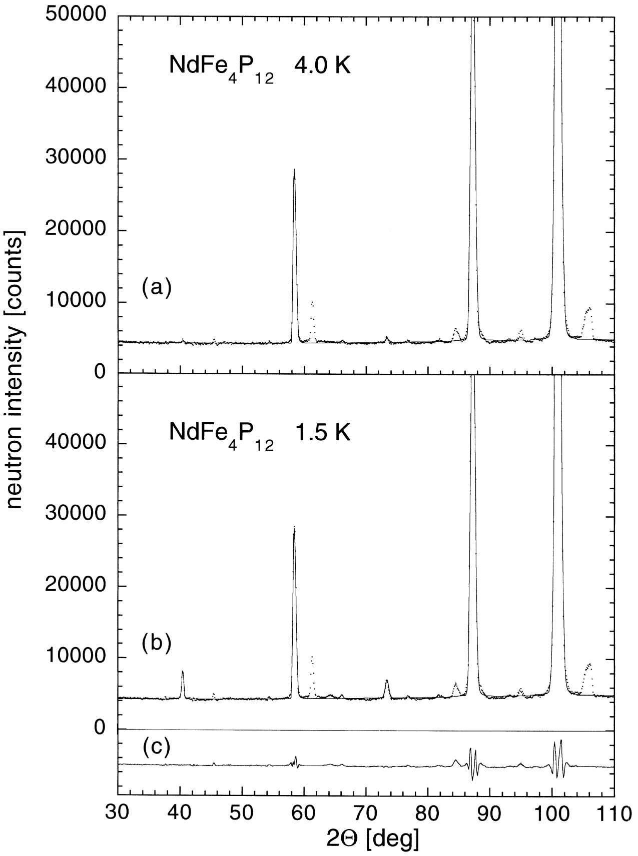

Fig. 4. (a) Neutron powder diffraction data of paramagnetic $NdFe_4P_{12}$ at 4 K, (b) low temperature neutron powder diffraction pattern at 1.5 K and (c) difference pattern of observed and calculated intensities for the refinement of the 1.5 K data. The additional peaks at $2\theta=61.3$ and 105.8° are due to an impurity phase and have been excluded for the fit.

experiments. Additional intensities at 1.5 K are due to long-range magnetic ordering. The magnetic peaks appear at the same positions as the reflections due to the chemical structure, which immediately reveals the ferromagnetic nature of the magnetic structure, i.e. $\mathbf{k}=[0,0,0]$. The simultaneous refinement of the low-temperature pattern with the chemical and ferromagnetic structure models describes the data well and the ordered Nd^{3+} magnetic moment at $T=1.5$ K turns out to be 1.61(7) μ_B. This value corresponds to the magnetic moments derived by magnetization measurements in Ref. [5] (1.74 μ_B/Nd at $T=2$ K and $H=5$ T) and those of Aoki et al. (Y. Aoki, T.D. Matsuda, H. Sugawara, H. Sato, unpublished results) (1.7 μ_B/Nd at $T=1.4$ K and $H=5$ T). As a consequence of the cubic crystal symmetry we cannot extract information about the orientation of the magnetic moments with respect to the crystal axis from our powder diffraction data. The temperature dependence of the magnetic (110) peak is shown in Fig. 5 and confirms the Curie temperature $T_C \approx 2$ K for the ferromagnetic ordering.

Similar measurements were performed on $PrFe_4P_{12}$. In contrast to the Nd compound no evidence for magnetic ordering was found. The measurement was repeated several times yielding a very good counting statistic and for our sample the previously proposed antiferromagnetic ordering below 6.2 K cannot be confirmed.

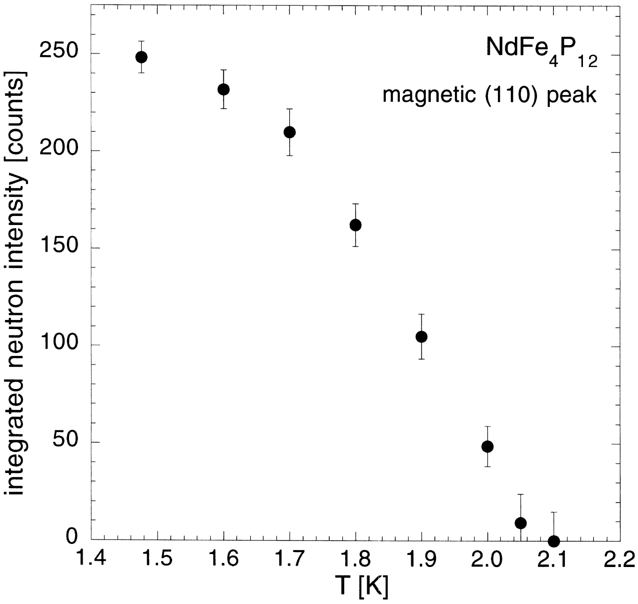

Fig. 5. $NdFe_4P_{12}$: temperature variation of the integrated neutron intensity of the magnetic (110) peak at $2\theta=40.4°$.

Being able to exclude long-range ordering of the Pr^{3+} dipole moments in $PrFe_4P_{12}$, there are quite a few possible explanations for the nature of the phase transition detected in macroscopic measurements, but not in neutron powder diffraction experiments. A detailed discussion of this interesting problem will be subject to future works.

4. Summary

We have presented a neutron powder diffraction study of the ternary rare-earth phosphides $PrFe_4P_{12}$ and $NdFe_4P_{12}$. The temperature dependence of the crystallographic structure was measured. The unusual behavior of the rare-earth Debye–Waller factor could directly be linked to large-amplitude thermal vibrations, consistent with speculations that the ion is weakly bound in an oversized atomic ‘cage’ formed in the filled skutterudite crystal structure. Finally the magnetic ordering phenomena in these compound were investigated. Whereas the proposed long-range antiferromagnetic ordering in $PrFe_4P_{12}$ could not be confirmed, $NdFe_4P_{12}$ orders ferromagnetically below $T_C=1.94$ K with an ordered Nd^{3+} moment of 1.61(7) μ_B at 1.5 K.

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