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Synthesis and Crystal Structure of a New Europium Nickel Phosphide Phase, $EuNi_5P_3$

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A new europium nickel phosphide compound $EuNi_5P_3$ was synthesized in a tin flux. The structure was refined from single crystal X-ray data in the space group Cmcm to an R value of 2.06%. The lattice parameters are $a = 3.5986(3)$, $b = 11.7374(8)$, and $c = 11.5230(10)$ Å and the compound is isotypic with $LaCo_5P_3$ and $LaNi_5P_3$. The room temperature magnetic moment of 8.1 Bohr magnetons indicates that the europium ions are in the +2 oxidation state.

Introduction

Two europium nickel phosphide compounds, $EuNi_2P_2$ and $Eu_2Ni_{12}P_7$, have been reported previously. $EuNi_2P_2$, like many rare earth transition metal phosphides and silicides of the same stoichiometry, crystallizes with the $ThCr_2Si_2$ structure (*1*). $Eu_2Ni_{12}P_7$ has the $Zr_2Fe_{12}P_7$ structure and is related to a large number of compounds in which the phosphorous atoms are coordinated to nine metal atoms in a tricapped trigonal prismatic arrangement (*2*). Here we report a new phase, $EuNi_5P_3$, which has the $LaCo_5P_3$ structure (*3*) and similar tricapped trigonal prismatic coordination about the phosphorus atoms.

Preparation

Single crystals of $EuNi_5P_3$ were prepared in a tin flux according to the methods described by Jeitschko and co-workers (*1–3*). Europium (4*N*), phosphorus (5*N*), nickel (5*N*), and tin (5*N*) were mixed in the ratio 1:2:2:20 and sealed in evacuated quartz tubes. The tubes were heated to 425°C for 6 hr, then to 900°C, cooled at 2 deg/hr to 575°C, and then cooled rapidly. After dissolution of the tin in hydrochloric acid, well-developed plates of $EuNi_2P_2$ and rods of $EuNi_5P_3$ remained.

Structure Refinement

Precession photos of single crystals of $EuNi_5P_3$ showed orthorhombic Laue symmetry. Single crystal intensity data were collected on an Enraf-Nonius CAD-4 diffractometer (*4*). Automatic peak search and indexing procedures yielded a monoclinic reduced primitive cell, but inspection of the Niggli values (*5*) revealed the C-centered orthorhombic cell, which was used for all further work. Cell and data collection parameters are summarized in Tables I and II. The C-centering was verified by collection

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and inspection of systematically absent data.

The 833 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects (*6*)[1,2]. Inspection of the azimuthal scan data[3] showed a variation $I_{\min}/I_{\max} = 0.57$ for the average curve. An absorption correction based on the measured shape and size of the crystal and an 8 × 8 × 14 Gaussian grid of internal points were applied to the data ($T_{\max} = 0.083$, $T_{\min} = 0.024$). Inspection of the systematic absences showed that all $h0l$ reflections with $l = 2n + 1$ were weak, but that some of them had intensities well above three times their esd. The systematic absences for the C-centering and the 2_1 axis along z were confirmed and there were no other systematic absences. Attempts to refine the structure in space group C222$_1$, however, failed to converge, so the final refinement was in Cmcm, with a required mirror plane at $x = 0$. Removal of systematically absent data left 423 unique data in the final data set.

TABLE I

CRYSTAL PARAMETERS AT 25°C[a,b]

$a = 3.5986(3)$ Å
$b = 11.7374(8)$ Å
$c = 11.5230(10)$ Å
$V = 486.7(1)$ Å^3
μ(calc) = 326 cm^{-1}
Size of crystal: 0.13 × 0.13 × 0.26 mm
Space group: Cmcm
Formula weight: 538.4 amu
$Z = 4$
$d_c = 7.35$ g cm^{-3}

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections with 2θ between 40° and 45°.

[b] In this and all subsequent tables the esd's of all parameters are given in parentheses. Right-justified to the least significant digit(s) given.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. In order to achieve convergent refinement a secondary extinction parameter (*7*) had to be refined from a very early stage in the structure solution process. The value of the extinction

TABLE II

DATA MEASUREMENT PARAMETERS

Radiation:	Mo Kα (λ = 0.71073 Å)
Monochromator:	Highly oriented graphite (2θ = 12.2°)
Detector:	Crystal scintillation counter, with PHA $+h$, $+k$, $+l$
2θ Range: 3° → 60°	Scan type: $\theta - 2\theta$
Scan width:	$\Delta\theta = 0.65 + .347 \tan(\theta)$
Scan speed:	0.78 to 6.7 (θ, °/min)
Background:	Measured over 0.25($\Delta\theta$) added to each end of the scan

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[1] All calculations were performed on a PDP 11/60 using a locally modified Nonius-SDP(10) software operating under RSX-11M.

[2] The data-reduction formulae are:

$$F_0^2 = \frac{\omega}{Lp}(C - 2B) \quad \sigma_0(F_0^2) = \frac{\omega}{Lp}(C + 4B)^{1/2}$$

$$F = \sqrt{F_0^2} \quad \sigma_0(F) = \frac{\sigma_0(F_0^2)}{2F_0}$$

where C is the total count in the scan, B the sum of the two background counts, ω the scan speed used in deg/min, and

$$\frac{1}{LP} = \frac{\sin 2\theta(1 + \cos^2 2\theta_m)}{1 + \cos^2 2\theta_m - \sin^2 2\theta}$$

is the correction for Lorentz and polarization effects for a reflection with scattering angle 2θ and radiation monochromatized with a 50% perfect single-crystal monochromator with scattering angle $2\theta_m$.

[3] Reflections used for azimuthal scans were located near $\chi = 90°$ and the intensities were measured at 10° increments of rotation of the crystal about the diffraction vector.

coefficient, g, was so large that many reflections had correction factors ($F_{\mathrm{corr}} = (1 + gI)F_0$) of 1.5 and greater. Since the Zachariasen approximation is not a good one for such large corrections or for such an anisotropic case, reflections having correction factors greater than 1.5 were progressively removed from the refinement. In the final cycles of least squares, 77 high-intensity reflections were removed for this reason. The maximum calculated correction factor after refinement was 2.0 for the (004) reflection. In addition, five more reflections with low I but very poor agreement were removed, and five reflections with essentially zero F_0 and large F_{clc} were noted. These are presumed to be due to instrumental error.

The final residuals for 32 variables refined against the 332 data for which $F^2 > 3\sigma(F^2)$ and $gI < 0.5$, were $R = 2.06\%$, $wR = 2.94\%$, and $GOF = 1.68$. The R value for all 423 data was 3.56%. The quantity minimized by the least-squares program was $\Sigma w(|F_0| - |F_c|)^2$, where w is the weight of a given observation. The p-factor[4] used to reduce the weight of intense reflections was set to 0.03 throughout the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used (*8*) and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion (*9*). A listing of the values of F_0 and F_c is available as supplementary material.[5]

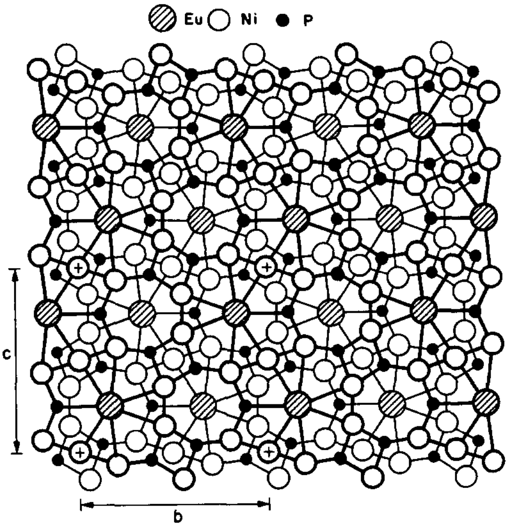

FIG. 1. ORTEP drawing of $EuNi_5P_3$. Atoms and connections drawn with heavy lines are at $a = \pm 0.5$, etc., with light lines at $a = 0.0$ and $a = 1.0$, etc. The crosses indicate Ni(1).

Discussion

$EuNi_5P_3$ is isotypic with $LaCo_5P_3$ and $LaNi_5P_3$ (*3*), the only other rare earth transition metal pnictides reported with this structure. The difference between the coordinates reported here and those in (*3*), $x, \frac{1}{2} - y, \frac{1}{2} - z$, corresponds to an origin shift of $0, \frac{1}{2}, \frac{1}{2}$ plus rotation about the 2-fold axis parallel to x. In $EuNi_5P_3$, the atoms lie in mirror planes at $x = 0, \frac{1}{2}, 1$, etc., as shown in Fig. 1. The positional parameters are in Table III, and Table IV contains a list of the distances between the various atoms. The coordination polyhedra about all the atoms are prisms capped on all rectangular faces. $P(1)$ and $P(2)$ each lie in a tri-capped isos-

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[4] $$R = \frac{\Sigma||F_0| - |F_c||}{\Sigma|F_0|} \qquad wR = \left\{\frac{\Sigma w(|F_0| - |F_c|)^2}{\Sigma w F_0^2}\right\}^{1/2}$$

$$GOF = \left\{\frac{\Sigma w(|F_0| - |F_c|)^2}{(n_o - n_v)}\right\}^{1/2}$$

where n_o is the number of observations, n_v the number of variable parameters, and the weights w were given by

$$w = \frac{4F_0^2}{\sigma^2(F_0^2)}, \quad \sigma^2(F_0^2) = \{\sigma_0^2(F_0^2) + (pF^2)^2\}$$

where p is the factor used to lower the weight of intense reflections.

[5] A table of the observed and calculated structure factors is available from the authors upon request.

TABLE III

TABLE OF POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom		x	y	z	B(Å^2)
Eu	4c	0.000	0.16181(2)	0.250	0.544(4)
Ni(1)	4a	0.000	0.000	0.000	0.50(1)
Ni(2)	8f	0.000	0.44886(4)	0.35526(5)	0.507(7)
Ni(3)	8f	0.000	0.19799(4)	−0.06768(4)	0.547(7)
P(1)	8f	0.000	0.38157(8)	−0.04066(9)	0.43(1)
P(2)	4c	0.000	−0.1168(1)	0.250	0.46(2)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(\frac{4}{3})*[a^2*B(1,1) + B^2*B(2,2) + c^2*B(3,3) + ab(\cos\gamma)*B(1,2) + ac(\cos\beta)*B(1,3) + bc(\cos\alpha)*B(2,3)]$.

TABLE IV

INTERATOMIC DISTANCES IN $EuNi_5P_3$

	Atom 1	Atom 2	Distance
2	P(1)	Eu	3.052(1)
2	P(1)	Ni(1)	2.321(1)
2	P(1)	Ni(3)	2.381(1)
	P(1)	Ni(2)	2.324(1)
	P(1)	Ni(2)	2.278(1)
	P(1)	Ni(3)	2.177(1)
2	P(2)	Eu	3.160(1)
4	P(2)	Ni(2)	2.303(1)
	P(2)	Eu	3.270(1)
2	P(2)	Ni(3)	2.307(1)
4	Eu	Ni(2)	3.310(1)
4	Eu	Ni(3)	3.219(1)
4	Eu	P(1)	3.052(1)
2	Eu	P(2)	3.160(1)
2	Eu	Ni(1)	3.450(1)
2	Eu	Ni(2)	3.581(1)
2	Eu	Ni(3)	3.685(1)
	Eu	P(2)	3.270(1)
4	Ni(1)	Ni(4)	4.546(1)
4	Ni(1)	P(1)	4.341(1)
2	Ni(1)	Eu	3.450(1)
2	Ni(1)	Ni(3)	2.451(1)
2	Ni(2)	Eu	3.310(1)
2	Ni(2)	Ni(1)	2.526(1)
2	Ni(2)	Ni(3)	2.645(1)
2	Ni(2)	P(2)	2.303(1)
	Ni(2)	Eu	3.581(1)
	Ni(2)	Ni(2)	2.426(1)
	Ni(2)	P(1)	2.324(1)
	Ni(2)	P(1)	2.278(1)
2	Ni(3)	Eu	3.219(1)
2	Ni(3)	Ni(2)	2.645(1)
2	Ni(3)	Ni(3)	2.676(1)
2	Ni(3)	P(1)	2.381(1)
	Ni(3)	Eu	3.685(1)
	Ni(3)	Ni(1)	2.451(1)
	Ni(3)	P(1)	2.177(1)
	Ni(3)	P(2)	2.307(1)

celes trigonal prism of nine metal atoms. This is a common coordination environment for phosphorus atoms in phosphides with high metal content (*10*) and is found also in $Eu_2Ni_{12}P_7$ (*2*) and YCo_5P_3 (*11*). Ni(2) and Ni(3) each lie in a tetra-capped kite-shaped prism and Ni(1) lies in a tetra-capped prism that is roughly rhomboidal. A hepta-capped heptagonal prism of nickel and phosphorous atoms surrounds each Eu atom. The coordination numbers are 9 for P, 12 for Ni, and 21 for Eu.

The similarity in cell volumes between $LaNi_5P_3$ (490.5 Å^3) and $EuNi_5P_3$ (486.7 Å^3) suggests that the Eu atoms are divalent. If the Eu atoms were trivalent, a smaller cell volume would be expected since trivalent Eu is smaller than trivalent La. We have confirmed the +2 oxidation state of the Eu atoms in $EuNi_5P_3$ by magnetic susceptibility measurements; the high-temperature magnetic moment was found to be 8.1 Bohr magnetons, in good agreement with the free ion value of 8.0 Bohr magnetons. The low-temperature magnetism of this compound shows interesting behavior which will be discussed in a future publication, along with the details of the magnetic measurements (*12*). In the related $Eu_2Ni_{12}P_7$ compound (*2*), the europium atoms are also divalent. $Eu_2Ni_{12}P_7$ differs from $EuNi_5P_3$ in the way in which the phosphorus-containing tri-capped trigonal prisms are linked together, and in the coordination about the

Eu, which is only 18 instead of 21. In contrast, the Eu atoms in the only other known phase, $EuNi_2P_2$, have fluctuating valence (*1*).

All of the other known LnM_5P_3 compounds, where *Ln* is a lanthanide element and *M* is Fe, Co, or Ni, have the YCo_5P_3 structure (*11*). An important difference between the YCo_5P_3 structure and the $LaCo_5P_3$ structure is the number of atoms coordinated to the lanthanide ions. The lanthanide atoms are trivalent in compounds with the YCo_5P_3 structure, and these smaller ions have a coordination number of only 18 instead of the coordination number of 21 observed for the divalent Eu atoms and the larger trivalent La atoms. Even though $Eu_2Ni_{12}P_7$ forms with 18 nearest neighbors coordinated to the divalent Eu atoms, it seems likely that $EuNi_5P_3$ does not crystallize with the YCo_5P_3 structure because of the large size of divalent Eu. $EuCo_5P_3$ also does not form with the YCo_5P_3 structure.

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Note added in proof. $EuNi_5P_3$ can also be prepared from a stoichiometric mixture in tin with the ratio of Eu : Ni : P : Sn equal to 1 : 5 : 3 : 20.

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