J. Phys. Chem. Solids Vol. 53, No. 5, pp. 687–690, 1992
Printed in Great Britain.

0022-3697/92 \$5.00 + 0.00
Pergamon Press plc

A NEUTRON DIFFRACTION STUDY OF THE MAGNETIC STRUCTURE OF $EuCo_2P_2$

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(*Received* 23 *September* 1991; *accepted* 16 *October* 1991)

Abstract—A 1.44 mm^3 single crystal of $EuCo_2P_2$, obtained from a tin flux was investigated by neutron diffraction. The $ThCr_2Si_2$ type nuclear structure was confirmed ($R = 0.08$ for 32 unique structure factors and six variable parameters). The magnetic structure was determined with a residual of $R = 0.10$ for 15 unique magnetic satellite reflections $h, k, l \pm 0.85$ and one variable parameter, the magnetic moment of the europium atoms: $\mu_{exp} = 6.9 \pm 0.1\ \mu_B$. The cobalt atoms are not magnetic. The magnetic moments of the europium atoms lie in the basal planes of the tetragonal cell. Their order is ferromagnetic within the planes. Along the c-axis the magnetic moments order to a slightly temperature dependent incommensurate antiferromagnetic spiral structure with a propagation vector of about $\mathbf{k} = (0, 0, 0.85)$. The Néel temperature of $T_N = 66.5 \pm 0.2$ K is in good agreement with that obtained from magnetic susceptibility measurements.

Keywords: Magnetic structure, neutron diffraction, single crystal, $EuCo_2P_2$.

1. INTRODUCTION

With the recently reported chromium compounds [1] more than 200 silicides are known with $ThCr_2Si_2$ structure [2, 3]. This body centered tetragonal structure is rather simple (Fig. 1) with only one crystallographic site for each atomic species and only one variable positional parameter, the z value of the Si site. Some 200 papers deal with the magnetic properties of these silicides and the corresponding germanides [4]. The isotypic phosphides were prepared much later [5 and references therein] and the investigations of their magnetic properties have started only recently. In the compounds LnT_2P_2 (Ln = lanthanoids, T = Fe, Co, Ni) with the trivalent rare earth elements magnetic moments at the transition metal sites were observed only for the cobalt containing compounds [6–8]. ^{151}Eu Mössbauer spectroscopy of $EuCo_2P_2$, however, suggested that the europium atoms are divalent and the magnetism of this compound was attributed essentially to the Eu^{2+} species [7], which is confirmed by the present study.

The results of the magnetic susceptibility measurements of $EuCo_2P_2$ were already reported [7]. The $1/\chi$ vs T plot is reproduced here (Fig. 2). It shows a minimum, indicating antiferromagnetism with a Néel temperature of $T_N = 67(\pm 1)$ K. Somewhat in contrast to this result the Weiss constant is positive ($\Theta_W = 20$ K), which usually suggests ferromagnetism. The magnetic structure reported here resolves this apparent contradiction. A brief account of this work was given before [9].

2. EXPERIMENTAL DETAILS AND RESULTS

Crystals of $EuCo_2P_2$ were prepared from a tin flux essentially as described earlier [7, 10, 11]. In order to obtain larger crystals the total weight of the sample was increased to about 5 g. The starting composition of the powder components with the atomic ratio of Eu:Co:P:Sn = 1.2:2:2:20 was annealed in evacuated silica tubes for 7 days at 880°C and slowly cooled (4°C h^{-1}) to room temperature. After dissolving the tin-rich matrix prismatic single crystals of $EuCo_2P_2$ were obtained with edge-lengths of up to 2 mm.

A single crystal of $EuCo_2P_2$ with a volume of 1.44 mm^3 was investigated on the four-circle diffractometer D9 at the reactor of the Institute Laue-Langevin in Grenoble with monochromated neutrons of wavelength $\lambda = 851$ (± 1) pm. The tetragonal symmetry of the crystals was confirmed by the neutron diffraction experiments. In agreement with the body-centered nuclear structure the peaks $h + k + l = 2n + 1$ were absent, however, magnetic superstructure reflections were observed as satellites of all allowed nuclear peaks h, k, l at the positions $h, k, l \pm 0.85$ in reciprocal space. The intensities of these

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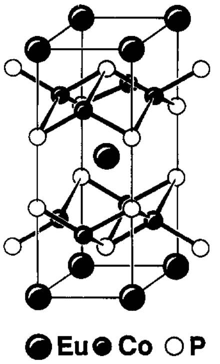

Fig. 1. The crystal structure of $ThCr_2Si_2$. In this structure the Th positions can also be occupied by alkaline earth, rare earth and actinoid atoms, the Cr positions are suited for all late transition metals and silicon can be substituted by boron, germanium, phosphorus as well as their heavier homologues.

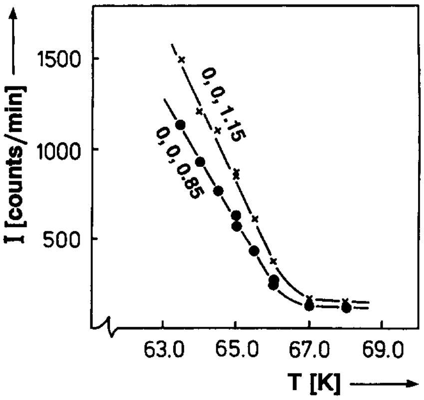

Fig. 3. Temperature dependence of the intensities of the magnetic reflections 0, 0, 0.85 and 0, 0, 1.15 of $EuCo_2P_2$. Because of the high background counts these reflections were not used for the refinement of the magnetic structure. They are therefore not listed in Table 1.

peaks decreased with increasing temperature. A Néel temperature of $T_N = 66.5(\pm 0.2)$ K was obtained from the extrapolation of the intensity data (Fig. 3), in good agreement with that of $T_N = 67(\pm 1)$ K calculated from the magnetic susceptibility and Mössbauer data [7]. The positions of these peaks were slightly temperature dependent. They varied from $\Delta l = 0.852 \pm 0.004$ at 15 K to $\Delta l = 0.834 \pm 0.004$ at 64 K. The tetragonal lattice constants of $a = 377(1)$ pm and $c = 1139(4)$ pm at 15 K were within one standard deviation the same as those previously observed at room temperature. A total of 32 unique nuclear and 15 magnetic structure factors were collected at 15 K for the structure determinations.

The structures were refined by full-matrix least-squares programmes [12] using the scattering lengths of $b = 2.50$ fm for cobalt and $b = 5.13$ fm for phosporus [13]. For the Eu atoms a value of $b = 6.8$ fm was used as a starting parameter [14]. It was varied during the refinement and a final scattering length of $b = 5.6$ (± 1.2) fm was obtained. Because of the limited data set the nuclear structure determination is less accurate than the previous structure determination from single-crystal X-ray data [10]. For the only positional parameter—the z parameter of the P atoms—a value of $z = 0.3571(8)$ was obtained, in good agreement with the previously determined value of $z = 0.3558(2)$. The final residual for the nuclear structure is $R = 0.08$ for six variable parameters (one positional, three thermal, the scale factor and the scattering length of Eu atoms) and 32 structure factors.

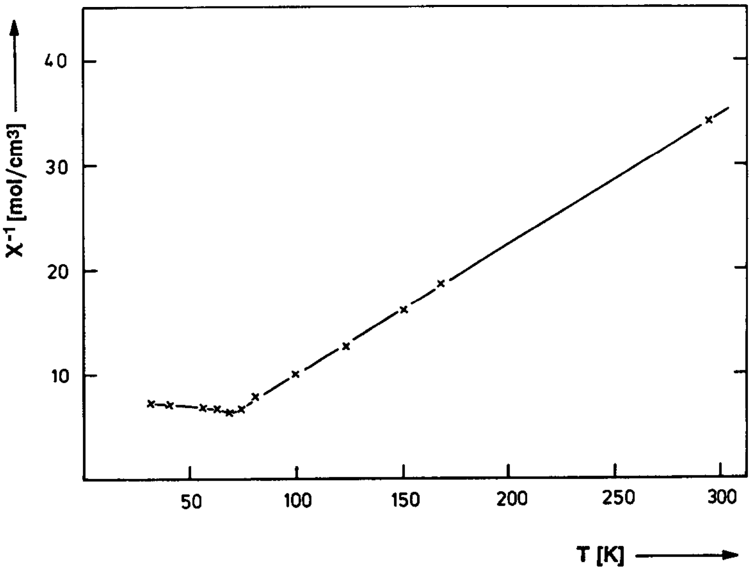

Fig. 2. Reciprocal magnetic susceptibility of $EuCo_2P_2$ as a function of temperature.

Table 1. Structure factors for the magnetic structure of $EuCo_2P_2$

h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}
0	0	2.85	102	110	1	0	3.85	66	80
0	0	3.15	100	107	1	0	4.15	66	79
0	0	4.85	85	89	1	0	5.85	60	67
0	0	5.15	79	86	2	0	0.85	52	54
0	0	6.85	56	68	2	0	1.15	52	54
1	0	0.15	79	76	2	0	2.85	49	54
1	0	1.85	74	82	2	1	1.85	59	49
1	0	2.15	68	83					

The existence of the magnetic peaks *hkl* at 0, 0, 0.85 and 0, 0, 1.15 (both satellites of the reflection 0, 0, 1, which is extinct in the body centered nuclear structure) suggested an incommensurate magnetic structure with ferromagnetic order of the magnetic moments within the basal plane of the tetragonal cell and a spiral structure along the *c*-direction. For the refinement of this model the magnetic form factor for the Eu atoms was taken from Freemann and Desclaux [15]. A magnetic moment of $\mu_{exp} = 6.9(\pm 0.1)\ \mu_B$ was obtained. It is in good agreement with the theoretical value of $\mu_{eff} = g\ J = 7.0\ \mu_B$ expected for Eu^{2+}. The final residual is $R = 0.10$ for one variable and 15 structure factors (Table 1).

3. DISCUSSION

The magnetic structure of $EuCo_2P_2$ is shown in Fig. 4. The magnetic moments of the Eu atoms are oriented perpendicular to the *c*-axis and form an incommensurate sinusoidal (or cosinusoidal—these descriptions are completely equivalent in this case) spiral with a propagation vector $\mathbf{k} = (0, 0, 0.85)$ and with the turning axis parallel to the *c*-axis. The Co atoms show no magnetic order. The order of the Eu moments is ferromagnetic within the basal planes in agreement with the positive Weiss constant obtained from the magnetic susceptibility measurements. Along the *c*-axis the order is that of an antiferromagnetic spiral and this agrees with the overall antiferromagnetic behaviour of the magnetic susceptibility. The wavelength of the modulation is about $1/0.85(=1.18)$ times larger than the *c*-axis of the nuclear structure. This ratio was found to be slightly dependent on temperature. The ratio of 1/0.834 found at 64 K is close to the ratio of 5/6(1/0.833), i.e. there are five translation lengths of the magnetic cell for six translation lengths of the nuclear structure. At 15 K this ratio was found to be 1/0.852, which is close to the ratio of 6/7. If this magnetic structure were to be maintained at still lower temperatures, it may lock in at exactly 6/7 (1/0.857). The ground state may then be called a commensurate structure with this ratio.

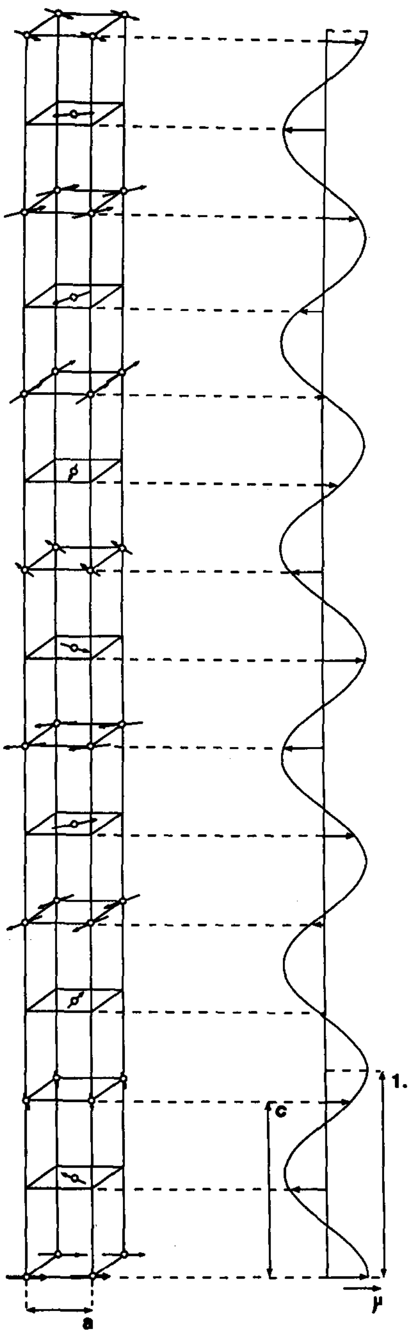

Fig. 4. Helimagnetic structure of $EuCo_2P_2$. The europium atoms of seven tetragonal $ThCr_2Si_2$ type cells are shown. Their magnetic moments lie in the basal planes and they order parallel within these planes. Between the planes the order is that of an antiferromagnetic spiral. The projection of the magnetic moments μ onto an *a*-direction follows a sinusoidal curve.

Szytuła and Leciejewicz have reviewed the magnetic structures of the $ThCr_2Si_2$ type silicides and germanides [4]. A great variety of different kinds of order were observed for the magnetic moments of the rare earth atoms. The kind of order found here for $EuCo_2P_2$ is of the type described before for $HoNi_2Ge_2$ [16]. It was also suggested as a likely possibility for $NdNi_2Si_2$ [17]. In these cases the propagation vectors are $\mathbf{k} = (0, 0, 0.76)$ and $\mathbf{k} = (0, 0, 0.885)$, respectively. $PrCo_2Ge_2$ [18], $PrNi_2Si_2$ [19] and $NdNi_2Ge_2$ [20] also have relatively simple modulated antiferromagnetic structures, but there both, the propagation vectors and the magnetic moments are parallel to the c-axis and the modulation is not in the orientation of the magnetic moments but in the magnitude of the moments. More complicated modulated structures are also known, most of them with nickel as transition metal component [4, 17, 21].

There is generally agreement that the factors mainly responsible for the magnetic ordering in the $ThCr_2Si_2$ type silicides and germanides are exchange interactions via the conduction electrons (RKKY theory) and crystal field effects [4, 16, 17, 22], however, how this comes about is less well understood. For the $ThCr_2Si_2$ type phosphides only one other structure is known so far: in $PrCo_2P_2$ the magnetic moments of the Pr atoms are parallel to the c-axis and order with a commensurate antiferromagnetic structure with a propagation vector of $\mathbf{k} = (0, 0, 1)$ [23]. The fact that most of the incommensurate magnetic structures of the silicides and germanides occur for the isoelectronic Ni compounds indicates the importance of the band structure. The total number of valence electrons per formula unit of 30 for $EuCo_2P_2$ and 31 for the $LnNi_2Si_2$ and $LnNi_2Ge_2$ series is indeed similar. However, a rigid band model cannot be used for the phosphides on the one hand and the silicides and germanides on the other hand. In $EuCo_2P_2$ ($c/a = 3.02$) the P atoms are far apart from each other (P–P distance 327 pm) [10], while the X (Si and Ge) atoms in the corresponding nickel compounds seem to be paired with bond distances of about 230–250 pm. This can be concluded from the low c/a ratios of these compounds of about 2.4 [17, 24, 25] and the fact that the c/a ratios correlate with the X–X distances [26]. The only positional parameter z was not determined accurately for the compounds $LnNi_2Si_2$. For the isotypic compounds $PrCo_2Si_2$ [27], $TbCo_2Si_2$ [27], $HoCo_2Si_2$ [28], $ErCo_2Si_2$ [29] and UNi_2Si_2 [30] the c/a ratios vary between 2.40 and 2.50 and the Si–Si distances cover the range between 244 and 263 pm. Incidentally of these compounds again only the nickel compound UNi_2Si_2 has an incommensurate magnetic structure.

Acknowledgements—We thank the Hoechst AG, Werk Knapsack for a gift of ultrapure red phosphorus and Dr G. Höfer (Heraeus Quarzschmelze) for silica tubes. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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