Nuclear magnetic resonance studies in rare earth ternary phosphides

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Abstract. The results of $^{31}$P Knight shift (KS) and spin-lattice relaxation time ($T_1$) measurements in the temperature interval 42–300 K are reported for the compounds RENi$_2$P$_2$ (RE = Ce, Eu, Yb) in order to understand the nature of the ground state in these compounds. KS results conclusively establish that all these compounds exhibit non-magnetic ground states. The temperature dependence of spin-fluctuation temperature ($T_m$) in each case is estimated from the measured data. For EuNi$_2$P$_2$ the values of $T_m$ above 77 K qualitatively agree with those obtained from Mössbauer and susceptibility data employing ionic interconfigurational fluctuation model, but disagree at lower temperatures.

Keywords. Nuclear magnetic resonance; rare earth ternary phosphides; Knight shift; spin-lattice relaxation.

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Ever since the phenomenon of valence instabilities has been realized in rare earth systems, there has been growing interest in the application of several experimental methods in understanding the nature of the ground state in these compounds (Lawrence et al 1981). Among these methods, nuclear magnetic resonance (NMR) occupies a special place, as it gives a lot of information about the static as well as the dynamic part of the 4f magnetism through the measurement of Knight shift (KS) and spin-lattice relaxation time ($T_1$) of a suitable non-magnetic nucleus, respectively. As a part of our programme on the application of NMR to such rare earth systems, we have investigated the compounds RENi$_2$P$_2$ (RE = Ce, Eu, Yb), crystallizing in the ThCr$_2$Si$_2$-type tetragonal structure. We have chosen this relatively new series of compounds because a lattice volume anomaly (figure 1) has been observed for Ce, Eu and Yb indicating a non-trivalent state of these ions in this series (Jeitschko and Jäberg 1980). It should be mentioned here that EuNi$_2$P$_2$ has been earlier identified to be an interesting intermediate valent compound with a non-magnetic ground state (Nagaranjan et al 1985). Therefore, from the systematics observed in the ThCr$_2$Si$_2$ type compounds, one would naively expect that CeNi$_2$P$_2$ and YbNi$_2$P$_2$ also should exhibit non-magnetic ground states. The present work is aimed at verifying this hypothesis microscopically by the measurement of $^{31}$P Knight shift. Another aspect of this work is to obtain an estimate of the spin-fluctuation temperature ($T_m$) from the measured $T_1$, KS and susceptibility ($\chi$) values and to compare such results with those obtained by traditional methods. Such academic exercises are helpful in understanding the validity of the models of valence fluctuation.

The samples were prepared as described in the literature (Jeitschko and Jäberg 1980).
Figure 1. The lattice volume as a function of rare earth (RE) atomic number in $\text{RENi}_2\text{P}_2$ series.

Figure 2. $^{31}\text{P}$ Knight shift as a function of temperature in $\text{CeNi}_2\text{P}_2$, $\text{EuNi}_2\text{P}_2$ and $\text{YbNi}_2\text{P}_2$. 
NMR KS and \( T_1 \) values in the temperature interval 4-2-300 K were obtained employing pulsed spectrometers.

The results of \(^{31}\text{P} \) KS and \( T_1 \) measurements are shown in figures 2 and 3 respectively. In the case of \( \text{CeNi}_2\text{P}_2 \) and \( \text{YbNi}_2\text{P}_2 \), KS is very small and nearly temperature-independent. This observation shows that in both the compounds, the ground state is non-magnetic. The non-magnetism of \( \text{CeNi}_2\text{P}_2 \) is presumably due to strong spin fluctuations and not due to zero-4f occupation number, as tetravalent metallic Ce compounds are ruled out. This is further supported by a large, but nearly temperature-independent susceptibility (\( \chi \)) (not reported in this paper). (However, we have observed an increase in \( \chi \) below 30 K, which is presumably due to magnetic impurities, in view of the absence of such a rise in the KS data). This conclusion is consistent with the observation of a double-peaked \( L_{III} \) edge x-ray absorption spectrum (Sampathkumaran 1984 (unpublished)) typical of intermediate valent, metallic Ce materials. At present, it is rather difficult to say whether the non-magnetism of \( \text{YbNi}_2\text{P}_2 \) is due to 4f\(^{14} \) configuration (Yb\(^{2+} \) state) or due to valence fluctuations as the observed magnitude of KS is too small to distinguish. Susceptibility studies are underway to clarify this point. For \( \text{EuNi}_2\text{P}_2 \), KS is very large and strongly temperature-dependent with a peak at about 40 K. The magnitude of KS clearly shows that 4f contribution to KS is the dominant one and this proves that the non-magnetic ground state is due to fractional 4f count. On the basis of these results, it was earlier (Sampathkumaran et al 1985) argued that the breakdown of the linear relationship between KS and \( \chi \) (with temperature as an implicit parameter) in intermediate valent materials is due to the formation of the 4f-conduction band hybridized ground state.
The temperature-dependent behaviour of $T_1$ is found to be different for the three samples. The values of $T_1$ for CeNi$_2$P$_2$ and YbNi$_2$P$_2$ are nearly the same at 300 K. For YbNi$_2$P$_2$, $T_1T$ is constant with temperature indicating that the contribution to the relaxation behaviour by conduction electrons is the dominant one (Korringa-relaxation). However, for CeNi$_2$P$_2$, though $T_1$ increases with decreasing temperature, the magnitude of the increase is smaller relative to the behaviour expected on the basis of constancy of $T_1T$ (that is, $T_1$ does not follow a continuous line). We, therefore, conclude that (magnetic) 4$f$ electrons tend to dominate the relaxation behaviour as the temperature is decreased in this compound. For EuNi$_2$P$_2$, the values of $T_1$ are very small relative to other two compounds, showing thereby the dominant contribution of 4$f$ electrons. In support of this, in Eu$_{0.05}$Y$_{0.95}$Ni$_2$P$_2$, $T_1$ at 300 K is found to be very large (about 10 msec). Above 77 K $T_1T$ is nearly constant (within 20%).

An NMR estimate of the spin-fluctuation temperature ($T_{\text{eff}}$) can be obtained from the measured values of KS, $T_1$, and $\chi$, following the idea that $h/\tau_{\text{eff}}$ obtained by the relation

$$(K^2T_1T)^{-1} \chi = 2\gamma^2 K_B \tau_{\text{eff}},$$

is a quantitative estimate of the temperature dependence of $T_{\text{eff}}$ (MacLaughlin et al.

![Figure 4](image-url)  
**Figure 4.** Effective spin correlation parameter (a measure of $T_{\text{eff}}$) as a function of temperature for CeNi$_2$P$_2$ and EuNi$_2$P$_2$. A smooth line drawn through the points in each case, is a guide to the eye.
1979). Here $\gamma_n$ is the gyromagnetic ratio. The values of $h/\tau_{\text{eff}}$ thus obtained are plotted in figure 4 for CeNi$_2$P$_2$ and EuNi$_2$P$_2$. For CeNi$_2$P$_2$, $h/\tau_{\text{eff}}$ is found to undergo a decrease with decreasing temperature. For EuNi$_2$P$_2$, $h/\tau_{\text{eff}}$ passes through a maximum above 100 K and this trend is in good agreement with that obtained from Mössbauer isomer shift and susceptibility data employing ionic interconfiguration fluctuation (ICF) model, thereby rendering support to the validity of ICF model at high temperatures. It should be remarked at this point that similar support to ICF model was rendered from Raman spectroscopic studies on EuPd$_2$Si$_2$ and EuCu$_2$Si$_2$ by Zirngiebl et al. (1985,1986). However, below 100 K, it appears that $T_{sf}$ as inferred from $h/\tau_{\text{eff}}$ goes through another maximum at 40 K (figure 4); this feature cannot be obtained from the ICF model (Nowik et al. 1985). It is interesting to note that this anomaly occurs at the same temperature where the $4f$-hybridized ground state is proposed to set in (Sampathkumaran et al. 1985). This anomaly may indicate that (i) the assumptions of ICF model are not valid at low temperatures and (ii) the relaxation mechanism is also modified as the pure ground state sets in. It will be very interesting to verify these conclusions by the measurements of quasielastic line width in neutron scattering, which is again a measure of $T_{sf}$ for CeNi$_2$P$_2$ and EuNi$_2$P$_2$.

To summarize, the present NMR KS studies clearly establish the non-magnetic nature of the ground state of CeNi$_2$P$_2$, EuNi$_2$P$_2$ and YbNi$_2$P$_2$. Our results are helpful in understanding the temperature-dependent spin-fluctuation behaviour and to test the reliability of the ionic ICF model. Neutron scattering studies are called for to confirm our conclusions in this respect. A detailed report along with our susceptibility results will be published elsewhere.

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