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Origin of Knight-shift anomaly in intermediate-valence compounds

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A strong anomaly in the expected linear relation between ^{31}P-NMR Knight shift and bulk magnetic susceptibility is observed at low temperatures for an intermediate-valence Eu-based compound, i.e., $EuNi_2P_2$. It is shown that this anomaly is not caused by crystalline–electric-field or lattice-volume effects. Instead, it is the result of the formation of the hybridized $4f$ conduction-electron ground state at low temperatures.

The application of nuclear magnetic resonance (NMR) to intermediate-valence (IV) rare-earth (RE) systems allows the study of both magnetic[1-12] and electrostatic[13] features of the phenomenon. Particularly, the measurements of the NMR Knight shift (KS) of a suitable nonmagnetic element in the compound of interest can substitute the bulk magnetic susceptibility (χ) in probing the demagnetization of the IV system at low temperatures. Owing to its microscopic nature, KS is practically not influenced by magnetic impurities. However, for all IV Ce and Yb systems studied to date through KS, with the exception[11] of $CeRu_2Si_2$, a breakdown of the well-known linear relation between KS and χ below a temperature $T_{\max}$, characteristic for the system, has been observed; $T_{\max}$ has been identified as the temperature at which χ exhibits a maximum.

Several mechanisms ranging from a temperature dependence of the hyperfine coupling constant due to either variations in the lattice volume or a crystalline–electric-field (CEF) splitting of the RE ionic states, to a new KS contribution from the hybridized $4f$/conduction-electron ground state at low temperatures, have been proposed,[6] but could not be proven experimentally up to now. We have therefore studied ^{31}P-NMR in the well known[14-16] IV compound $EuNi_2P_2$ in the temperature range from 300 to 5 K, since CEF effects are expected to be negligible in Eu systems. We observe negative KS values, with maximum magnitude (4.2%) at 40 K, saturating at a smaller magnitude (3.8%) below 20 K. Above 40 K, a strictly linear relation between KS and χ is observed, which breaks down at lower temperatures. It should be mentioned here that ^{31}P-NMR KS studies have been performed[8] previously on $EuNi_2P_2$ above 77 K and could, therefore, not address the question of Δ_{KS}/χ anomaly below $T_{\max}$, where Δ_{KS} is the Knight shift. A comparative view of the KS anomaly found in the present work with previous results for IV Ce and Yb compounds strongly suggests that these effects are not due to lattice-volume anomalies. Instead, the KS anomaly seems to be caused by an additional KS contribution associated with the formation of the hybridized $4f$/conduction-electron ground state in such IV systems at low temperatures.

The sample was prepared by direct reaction of the constituent elements in an evacuated quartz tube as described in the literature,[17] and characterized by x-ray diffraction and Mössbauer spectroscopy. The absence of any satellite component in the ^{151}Eu-Mössbauer spectra measured between 5 and 300 K proves the homogeneous IV character of all Eu ions in this sample. The ^{31}P-NMR KS measurements were performed in an external field of 0.55 T at temperatures between 5 and 300 K employing a wideline NMR spectrometer. Owing to vanishing electric-quadrupole interaction (nuclear spin $I=\frac{1}{2}$), the ^{31}P NMR resonance is particularly suited to NMR measurements.

The results on the Knight shift with reference to the ^{31}P-NMR resonance position in H_3PO_4 are shown in Fig. 1 as a function of temperature. The NMR signal could be followed to the lowest temperature (5 K) measured. To our knowledge, NMR studies of Eu-based systems had previously not been performed to liquid-He temperatures. We find that $|\Delta_{KS}|$ increases with decreasing temperature, attaining a large, maximum value at 40 K (4.2%), and then decreases to 3.8% at 20 K (and below). The observation of the NMR signal in an external field at the lowest measured temperature supports earlier conclusions on the nonmagnetic ground state of $EuNi_2P_2$.[8,15]

We now compare the temperature dependence of KS with that of χ reported earlier.[15] In general, in rare-earth intermetallics, the $4f$ part of KS measured at a nonmagnetic site is a quantity linearly related[18] to χ via the relation

$$\Delta_{KS}(T)=\frac{H_{\mathrm{hf}}}{N\mu_B}\chi=c\chi \quad . \tag{1}$$

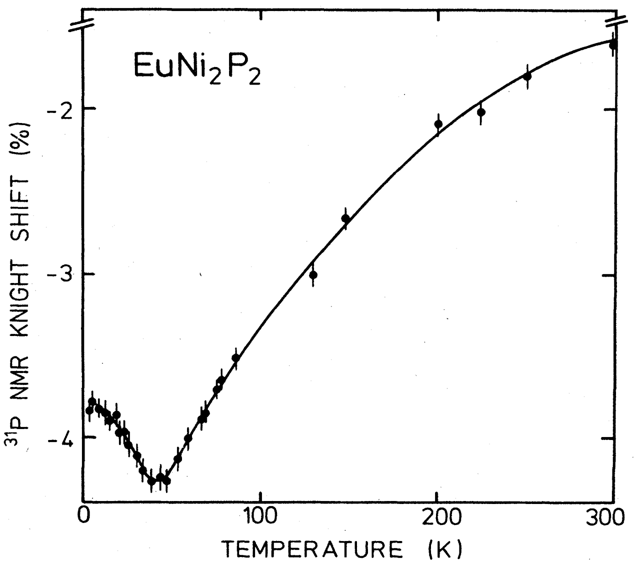

FIG. 1. ^{31}P-NMR Knight shift in $EuNi_2P_2$ as a function of temperature. The line through the points is a guide to the eye.

Here H_{hf} is the transferred hyperfine field, c the proportionality constant, N the Avogadro number, and μ_B the Bohr magneton. In order to check this relation, we have plotted in Fig. 2 KS vs χ (with temperature as an implicit parameter). We have not subtracted the non-$4f$ part K_0 of KS from the experimental data, as this contribution is normally small ($\leq 0.2\%$)[5,18] and temperature independent in the studied temperature range. Above $T_{\max}$, a linear relationship between KS and χ is observed. The value of KS corresponding to zero susceptibility is found to be $\cong 0.2\%$, representing a good estimate for K_0. The value of H_{hf} obtained from the slope of the straight line in Fig. 2 is $\cong 5.96$ kOe/μ_B.

However, there are several data points in Fig. 2 that do not lie on the straight line, and these correspond to temperatures below $T_{\max}$. Whereas χ decreases by less than 3% from $T_{\max}$ to 5 K, $|\Delta_{\mathrm{KS}}|$ reduces itself by 10%. The size of the deviation $\Delta K(5\text{ K}) = \Delta_{\mathrm{KS}}^{\mathrm{obs}}(5\text{ K}) - \Delta_{\mathrm{KS}}^{\chi\,\mathrm{lim}}(5\text{ K})$ is larger than the value of K_0. We also want to point out that there is no low-temperature rise due to the magnetic impurities in the susceptibility[15] of $\mathrm{EuNi_2P_2}$ used here and hence the KS anomaly in this compound is intrinsic. We therefore conclude that there is a positive contribution to the Knight shift developing at such low temperatures, similar to what has been reported for Ce- and Yb-based mixed-valence systems.[1-4,6] We will argue below that the observation of a breakdown of the linear relation between KS and χ in an Eu-based IV system eliminates conclusively the possible role of crystalline-electric field and/or lattice expansion/contraction of this KS anomaly.

In $\mathrm{CeAl_2}$, the trivalent Ce ions undergo CEF splitting, and it was observed that the KS of Al does not track χ below a temperature of the order of the CEF splitting.[19] It was argued that the hyperfine coupling constant in Eq. (1) is different for various CEF states, and the thermal population of these states alters the effective hyperfine coupling. At first glance, this reasoning appears plausible for Ce and also for Yb IV systems. Such an explanation, however, does not hold for Eu systems, since there are negligible CEF effects expected for both valence states of Eu. Eu^{2+} is spherically symmetric, and for Eu^{3+}, $J=0$ is the ground state, and states with $J \geq 2$ lie above 1400 K.

A further possible explanation proposed earlier[6] is connected with the influence of thermal contraction or expansion below $T_{\max}$. As KS is being measured at a non-rare-earth site, the hyperfine-coupling constant (H_{hf}) is expected to be a function of the distance between the RE and the NMR nucleus, i.e., the lattice volume. It has been shown previously that the transferred hyperfine field usually increases with decreasing volume.[20,21] For IV Ce-based systems, like $\mathrm{CeSn_3}$, a thermal contraction of the lattice is expected for decreasing temperatures (as the result of an increase of the valency of Ce), whereas for IV Yb-based systems, the reverse is the case.[22] Therefore, one would expect that, for $T < T_{\max}$, the hyperfine-coupling constant in Ce systems [i.e., the proportionality constant c in Eq. (1)], should increase, whereas for Yb systems, c should decrease. That is, ΔK should be positive in both cases, keeping the experimentally observed signs of KS in mind. This is indeed found to be true for the KS values of $^{119}\mathrm{Sn}$ in $\mathrm{CeSn_3}$,[1] of $^{29}\mathrm{Si}$ in $\mathrm{CeCu_2Si_2}$,[4] of $^{27}\mathrm{Al}$ in $\mathrm{YbAl_3}$,[2] and of $^{27}\mathrm{Al}$ in YbCuAl.[3] If this explanation should be true, the dependence of c on temperature for $\mathrm{EuNi_2P_2}$ should be similar to that of $\mathrm{CeSn_3}$, as the lattice of $\mathrm{EuNi_2P_2}$ shrinks due to the increasing population of the smaller Eu^{3+}-ionic states with decreasing temperature.[15,16] In other words, c should increase below $T_{\max}$ and hence ΔK should be negative for $\mathrm{EuNi_2P_2}$, contrary to the experimental observation (see Fig. 2).

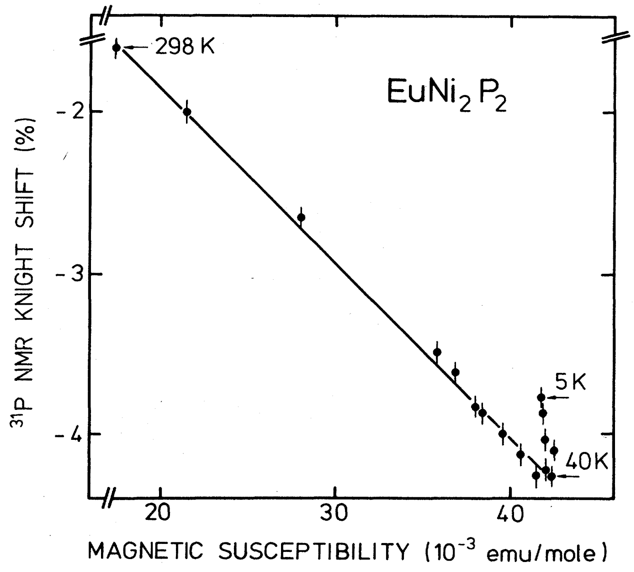

FIG. 2. Plot of the ^{31}P-NMR Knight shift vs the magnetic susceptibility (Ref. 14), with temperature as an implicit parameter. A continuous line is drawn through the data points where the linearity between KS and χ is valid.

A further argument ruling out the lattice-volume mechanisms as the origin of the KS anomaly is provided by the muon Knight shift in $\mathrm{CeSn_3}$, reported recently.[23] It has been found that there is an additional negative contribution to the muon Knight shift in $\mathrm{CeSn_3}$, contrary to what was reported for the $^{119}\mathrm{Sn}$-NMR KS in the same system.

In this way, we arrive at the conclusion that neither the CEF nor lattice-volume changes can universally explain the NMR-KS anomaly. Rather, we propose that a common mechanism should be operative in all these IV RE systems. Our conclusion is consistent with the hypothesis[6] that the observed KS anomalies are mainly due to the formation of $4f$ conduction-band hybridized ground states at low temperatures, causing a modification of the hyperfine-coupling constant at temperatures below $T_{\max}$. The temperature $T_{\max}$ has then a real physical significance, as often postulated, namely, indicating the onset of this state.

We finally would like to mention that there were considerable difficulties in observing the ^{31}P-NMR signal in the temperature range from 20 to 40 K due to a strong broadening of the resonance. This behavior should be compared with the maximum in the linewidth of the ^{151}Eu-Mössbauer resonance in the same compound around 40 K.[15] A common mechanism, possibly due to inhomogeneities in the valence of the Eu ions around 40 K, may be responsible for this behavior.

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