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Observation of a Fully Localized $3d^9$ Configuration for Nickel Ions in Alkali Metals

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The local susceptibilities and the $3d$ spin dynamics of isolated nickel ions in various alkali-metal hosts have been measured, utilizing the method of perturbed γ-ray distribution after recoil implantation. In the heavy alkali-metal hosts Cs, Rb, and K, the local susceptibilities of the isolated Ni ions show the temperature behavior of a fully localized spin-orbit-coupled $3d^9$ configuration. Clear host dependence of the magnetic behavior is seen in the spin-fluctuation rates which increase with decreasing host volume. In Na, the magnetic behavior drastically deviates from that of the purely ionic configuration, and Ni ions in Li as well as in Ca and Ba hosts are nonmagnetic.

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In recent years the question of localization of electrons in the partially filled shells of transition metals has again become a subject of considerable interest. Following the table of transition elements by Smith and Kmetko,[1] the degree of localization is the discriminating parameter for many bulk properties. The magnetism of most $4f$ metals is known to be determined by localized electrons, whereas many d elements are strongly influenced by band structure and hybridization effects. Marking the change between localized and itinerant d and f electrons, the intermediate region, comprising, e.g., Ce and Fe, and Co and Ni, is rendered prominent by an extreme complexity of all-important bulk quantities.

In the field of dilute magnetic alloys, the search for local moments is guided by the idea that magnetic moments will develop if the interaction of electrons "inside" one impurity atom survives hybridization or crystal fields. As nickel is estimated to have the strongest spin-orbit coupling and exchange interaction in the $3d$ series,[2,3] a well-defined local magnetic moment might be expected in some metallic hosts, yet no such observation has been published.

So the question arises whether nickel impurities will develop a fully localized configuration when incorporated in extreme environments. One such extreme system, which is characterized by sharp contrasts in atomic volume, electronegativity, and density of states between the constituents, has already been studied, Fe impurities in the alkali metals Cs, Rb, and K.[4] Here the isolated iron impurities are divalent and exhibit an unperturbed spin-orbit-coupled $3d^6$ configuration. Another question of interest is the actual ionic configuration of the Ni ions in the host. Estimates on the basis of a Born-Haber cycle[5] suggest that Ni might be monovalent in the alkali metals and, even more interesting, might display charge fluctuations.

In many metallic hosts Ni impurities show nonmagnetic behavior; in NiPd alloys, however, a positive magnetic hyperfine field has been found.[6-9]. This has been explained by negative core and positive orbital contributions and, in addition, transferred fields from neighboring Pd atoms, but it is not an indication of an unperturbed well-defined moment. For Fe impurities, local orbital moments are thought to be typical for sp-element metallic hosts, whereas pure spin magnetism is observed in d-metal hosts.[10] Elsewhere, $3d$ systerms such as Co in Au[11] and Fe in Ca[12] have been interpreted in terms of ionic configurations.

The observation of the perturbed angular distribution of γ rays[13] after recoil implantation is well suited to study local magnetic behavior. In this method, a radioactive atom is produced in a thin target foil by a nuclear reaction and implanted into a suitable host utilizing the recoil energy of the reaction. Thus impurity-host systems can be produced containing impurities at extreme dilutions ($\ll 1$ ppm) which cannot be made by standard methods.

In this Letter we describe the implantation of ^{63}Ni ions into alkali-element hosts and the measurements of the local magnetic fields at the impurity site. The ^{63}Ni probe nuclei are produced and aligned with the $^{48}\mathrm{Ca}(^{18}\mathrm{O},3n)^{63}\mathrm{Ni}$ reaction in a 1-mg/cm^2-thin ^{48}Ca foil. The pulsed ^{18}O beam of an energy of 45 MeV is provided by the heavy-ion accelerator VICKSI at the Hahn-Meitner-Institute in Berlin. The recoil energy of the probe atoms of about 10 MeV is high enough to ensure deep implantation of up to 10 μm into the host material directly behind the target foil. The target assembly is mounted on the cold copper tip of a He cryostat, providing temperatures between 20 and 400 K. The 5-mm-diam target is positioned in the beam focus where the external magnetic field B_{ext} of either a conventional electromagnet or the superconducting 10-T split-pair magnet SULEIMA[14] can be applied.

In the nuclear reaction, two isomeric levels in ^{63}Ni are populated: the $\frac{5}{2}^-$ level at 86.9 keV with a lifetime of $\tau=2.49(5)$ μs and a nuclear g factor of $g_N=+0.300(1)$,[15] and the $\frac{9}{2}^+$ level at 1.294 MeV, having a lifetime of $\tau=13.5(5)$ ns and a g factor of $g_N=-0.269(3)$.[8] Spin-rotation spectra $R(t)$ of the decaying isomers are measured as a function of temperature in magnetic fields of $B_{\mathrm{ext}}=1.1$, 1.5, and 1.8 T for the long-

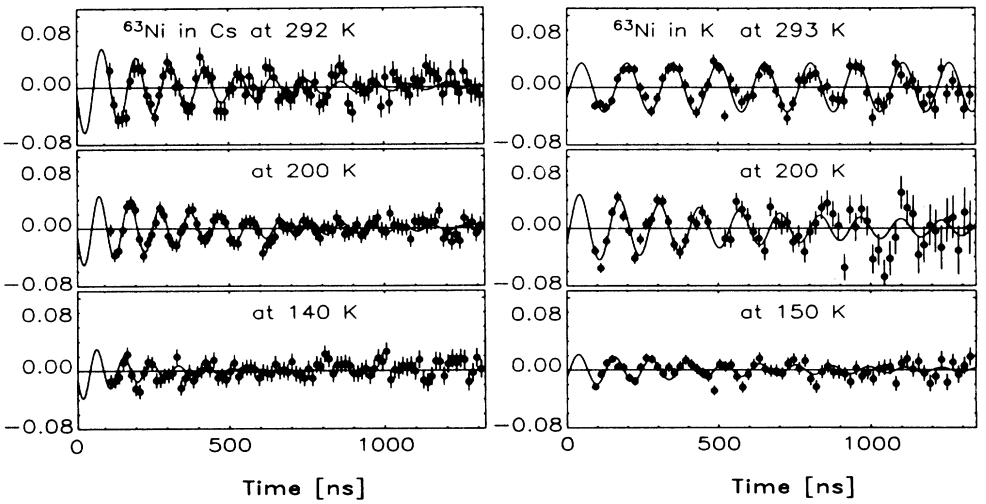

FIG. 1. Spin-rotation spectra of ^{63}Ni ($\frac{5}{2}^-$ level) in cesium and potassium hosts. External magnetic fields of $B_{\text{ext}}=1.5$ and 1.1 T have been used.

lived isomer and $B_{\text{ext}}=8.0$ T for the short-lived one. Examples are shown in Fig. 1.

From the spin-rotation spectra, the Larmor frequencies $\omega_L(T)$ are determined, which are the product of the nuclear magneton μ_N, the nuclear g factor g_N, and the magnetic field at the nucleus $B(T)=B_{\text{hf}}(T)+B_{\text{ext}}$: $\omega_L(T)=-[\mu_N g_N B(T)]/\hbar$. The paramagnetic enhancement factor $\beta(T)=1+B_{\text{hf}}(T)/B_{\text{ext}}$ is used to parametrize the measured hyperfine fields. In addition, the damping of the spin-rotation pattern contains information about the fluctuation times of the local moments.

The $\beta(T)$ values obtained in the measurements are displayed in Fig. 2 where reanalyzed data from an unpublished Ni*Cs* measurement[16] are also included. The temperature dependence of $\beta(T)$ closely follows a Curie law, $\beta-1\sim C/T$, for Ni in Cs, Rb, and K, the Curie constant being the same for all three hosts. For Ni in Na, the drastically reduced enhancement factor $\beta(T)$ indicates unstable magnetic behavior with $\beta(T)$ increasing from 1.02 at 30 K to about 1.11 at room temperature. Nickel in Li, as well as nickel in the alkaline earths, Ba and Ca, displays nonmagnetic behavior ($\beta=1$ for all temperatures).

The interpretation of the observed large positive $\beta(T)$ values for nickel in Cs, Rb, and K necessarily requires the assumption of local magnetic moments with strong orbital contributions. The discussion may be restricted to $3d^8$ or $3d^9$ configurations, each coupled according to Hund's rules. The paramagnetic enhancement factor can then be calculated from the saturation hyperfine field $B(0)$, the Landé factor g_J, and the total angular momentum J of the ground-state multiplet according to[17]

$$\beta(T)=1+[g_J\mu_B(J+1)B(0)/3k_BT]\,. \qquad (1)$$

Here the saturation field $B(0)$ can be expressed by the sum of a contribution $B_J(0)$ due to the $3d$ angular momentum and a term $B_s(0)$ which stems from the polarization of core s electrons. The $3d$ term to the hyperfine field may be related to the radial expectation value $\langle r^{-3}\rangle_{3d}$ via $B_J(0)=2\mu_B\langle r^{-3}\rangle_{3d}\langle J||N||J\rangle$ where $\langle J||N||J\rangle$ is the reduced matrix element of the angular part of the hyperfine operator. Values for $\langle r^{-3}\rangle_{3d}$ have been determined by Olsson and Rosén.[18] For the $^2D_{5/2}$ ground-state multiplet of the Ni^{1+} ion with $L=2$, $S=\frac{1}{2}$, $J=\frac{5}{2}$, and $g_J=\frac{6}{5}$, one obtains $B_{5/2}=114$ T. To estimate $B_s(0)$, we use $B_s\sim(-12.6\text{ T})2S$,[3,19] yielding $B_{1/2}(0)=-12.6$ T. The solid straight line in Fig. 2 bearing the indication for a $3d^9$ configuration is calculated with these parameters.

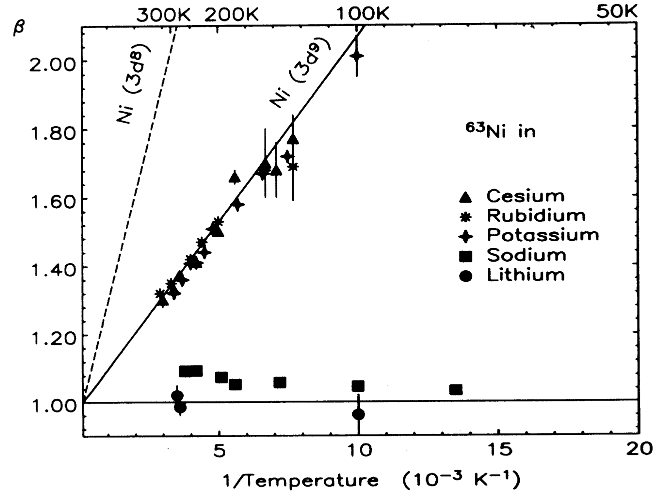

FIG. 2. Paramagnetic enhancement factors $\beta(T)$ for isolated Ni ions in different alkali metals as a function of temperature. The straight lines represent the temperature dependences calculated for ionic $3d^8$ and $3d^9$ configurations.

The expected temperature dependence for the $3d^8$ configuration is depicted in Fig. 2 as a dashed line. Here the saturation field for the Ni^{2+} ground-state multiplet $^3F_4$ ($L=3$, $S=1$, $J=4$, $g_J=\frac{5}{4}$) is calculated to be $B_4(0)=229$ T.

The agreement between the experimental values and those expected for the $3d^9$ configuration clearly indicates the existence of a spin-orbit-coupled ground state with an angular momentum of $J=\frac{5}{2}$ at the Ni^{1+} ion irrespective of the host for Cs, Rb, and K. The assumption of an unquenched but decoupled orbital moment $L=2$ can be excluded in view of the results for Fe in alkali metals,[4] since the spin-orbit coupling strength should grow going from Fe to Ni.[2,3] The strength of crystal fields, estimated in the weak-interaction limit,[20] is found to be smaller than 170 K if one attributes the observed small deviations of the $\beta(T)$ values from the Curie behavior exclusively to crystal-field splittings. In conclusion, we emphasize the fact that an unperturbed spin-orbit-coupled moment of localized d electrons exists at Ni impurities in the heavy alkali metals and that Ni is monovalent in these environments.

The partial demagnetization for Ni in Na cannot be unambiguously explained at the moment. The weak shift at low temperatures ($\beta\sim 1.02$) might indicate a nonmagnetic ground state and the drastic increase of $\beta(T)$ at about $T\sim 200$ K suggests that magnetic states are activated. Neither the Kondo type of demagnetization, which was estimated using the calculations of Rajan,[21] nor the valence-fluctuation model of Newns and Read[22] is able to explain the drastic increase of $\beta(T)$ which has been found in this measurement.

Now we turn to discuss the unexpected finding of host-dependent relaxation times for Ni ions in alkali metals. For a stable configuration, information on hybridization and $3d$ mixing can be extracted from the measured nuclear relaxation rate τ_N^{-1} through the relation[23,24]

$$\tau_N^{-1}=2(\mu_N/\hbar)^2(J+1)J^{-1}g_N^2B_J^2(0)\tau_J\,, \tag{2}$$

where τ_J is the electronic spin-fluctuation time. Because of spin fluctuations, the direction of the saturation field $B_J(0)$ changes quickly and leads to the nuclear spin relaxation, which is directly determined from the damping of the nuclear spin alignment in the spin-rotation spectra. In applying Eq. (2), other sources of the damping, such as electric quadrupolar interactions, are assumed to be negligible for the small Ni ions in the spacious alkali lattice, even if there is some radiation damage in the probe-ion environment.

The results exhibit the following remarkable features (cf. Fig. 3):

(i) The spin-fluctuation rates for Ni in Cs, Rb, and K hosts are distinct. This finding reveals a dependence of the local magnetism on host parameters, which does not manifest itself in the paramagnetic enhancement factor. In comparison, the rates for Fe have been found to be identical irrespective of each of these hosts.[4]

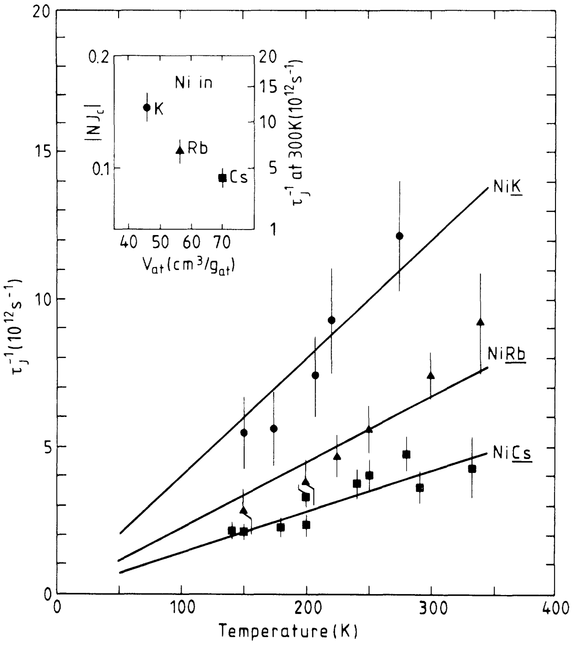

FIG. 3. Spin-relaxation rates τ_J^{-1} for Ni in Cs, Rb, and K. A linear temperature dependence of τ_J^{-1} is expected from the Korringa relation. Inset: dependence of τ_J^{-1} on the host volume.

(ii) The spin-fluctuation rates are unusually low, being $4\times10^{12}\ s^{-1}$ for Ni in Cs, $7\times10^{12}\ s^{-1}$ for Ni in Rb, and $12\times10^{12}\ s^{-1}$ for Ni in K at a measuring temperature of 300 K. From the uncertainty relation, linewidths of about 2.5, 4.5, and 8 meV, respectively, can be deduced. Thus, Ni is as stable as Fe in Cs, with linewidths as small as are usually observed in rare-earth systems.[25]

(iii) Within the error, the τ_J^{-1} rates show a Korringa-type linear temperature behavior, $\tau_J^{-1}=4\pi h^{-1}\times[N(E_F)J_c]^2k_BT$.[26] The proportionality constant can be determined by the product of host density of states $N(E_F)$ at the Fermi level and the effective exchange integral J_c. Rough estimates for the three alkali-metal hosts give values for $|N(E_F)J_c|$ of 0.09, 0.12, and 0.16, respectively, which, within the uncertainty of the measurement, scale with the inverse of the host-cell volume squared.[27-29]

In conclusion, the temperature behavior of the paramagnetic enhancement factors for Ni in the alkali-metal elements Cs, Rb, and K reveal the existence of fully localized $3d$ electrons of monovalent Ni ions. Small hybridization of the local $3d$ states with the conduction band at the Fermi level is found through the spin-fluctuation rates.

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