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Anomalously Small Knight Shift and Relaxation Rate in the Nonalloying System: Isolated Yttrium Ions in Liquid Rubidium

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Time-differential and stroboscopic measurements of the perturbed angular γ-ray distribution for isolated ^{88}Y ions in liquid Sr and Rb are reported. A drastic drop in the Knight shift and the nuclear relaxation rate is observed as the Sr matrix is replaced by Rb. This implies an almost vanishing density of $5s$ states on the Y ion in Rb at the Fermi level. A volume expansion of the Y Wigner-Seitz cell is suggested as the mechanism causing this anomalous behavior in *Rb*Y.

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In the last few years some progress has been made in understanding the electronic structure of disordered systems, particularly of those liquid metals which show a metal-nonmetal transition.[1,2] The nature of such transitions is a main topic of current interest. Several models have been developed to investigate the central problem: What are the mechanisms for the changes of electronic structure which, in a few cases, could be directly observed by microscopic measurements?[1,3] It seems that there is a whole spectrum of different mechanisms leading to the general phenomenon of metal-nonmetal transitions.[1-4]

In this Letter we report the first observation of almost vanishing s-conduction-electron density at the Fermi level on a transition-metal ion in a metallic host. The phenomenon occurs for Y in a liquid Rb matrix whereas the s states reflect normal behavior for liquid *Sr*Y. The nonalloying systems *Rb*Y and *Sr*Y were made accessible by nuclear reactions which (i) lead to extremely dilute Y ions (concentration <1 ppm) in the liquid hosts and (ii) excite and orient the long-lived 8^+ nuclear isomer in ^{88}Y which serves as an ideal magnetic microscopic probe for the measurements of the static and dynamic response by perturbed angular γ-ray distribution (PAD) techniques. We were forced to improve the accuracy which had been hitherto obtained in γ-ray PAD experiments by an order of magnitude to measure the Knight shift, K, for *Rb*Y. The most surprising result is that both K and the magnetic relaxation rate τ_m^{-1} are extremely small for the system *Rb*Y. We suggest that this anomalous behavior is mainly caused by a drastic difference in volume between the Y and Rb ions.

Isolated ^{88}Y ions were produced by the reactions ^{87}Rb(α, $3n$) and ^{88}Sr(d, $2n$) in liquid (and solid) Rb, liquid Sr, and in a saturated solution of RbOH in H_2O with use of pulsed α and d beams provided by the cyclotron at the Kernforschungszentrum Karlsruhe. The Rb target was kept under high vacuum in Pyrex glass whereas Sr was kept in a tantalum crucible. The γ-ray anisotropy of the 8^+ isomer[5] ($T_{1/2}=14$ ms, $g_N=0.60$) in ^{88}Y was observed in an external field, $B_{\rm ext}$, perpendicular to the beam-γ-detector [NaI(Tl)] plane.

Spin-lattice relaxation times τ_R were measured time differentially by the TDPAD method.[6] Examples are shown in Fig. 1. As a consequence of the very long half-life of the 8^+ isomer, one is forced to measure the TDPAD spectra at very small $B_{\rm ext}$ values ($\lesssim 10$ G) which in turn limits the accuracy of the nuclear Larmor frequencies ω_L.

Therefore, the Knight shifts were investigated by the stroboscopic observation of the perturbed angular γ-ray distribution (SOPAD).[7] The reso-

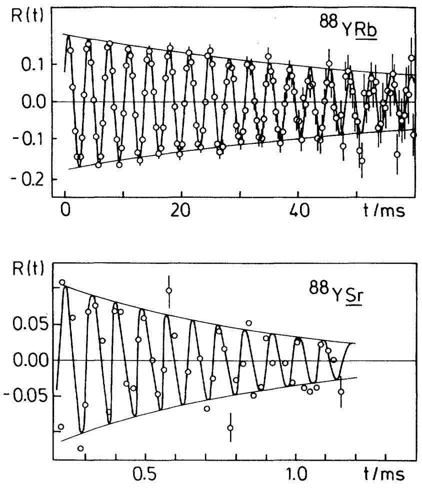

FIG. 1. TDPAD pattern of ^{88}Y in liquid Rb at 740 K (232 keV, 0.3 G) and in liquid Sr at 1180 K (443 keV, 13 G). The values in parentheses correspond to the γ lines and external fields used. The relaxation times are given by the damping of the precession.

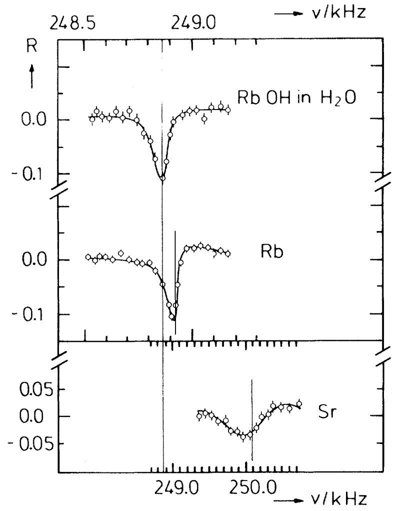

FIG. 2. Stroboscopic resonances of the perturbed angular distribution of the 443-keV γ rays of ^{88}Y in different hosts as a function of the inverse repetition time ν of the beam. The resonance points $\omega_L/\pi=\nu$ are marked by vertical lines. The solid lines represent the fits to the data as described in Ref. 9. The broader linewidth for *Sr*Y results from the shorter relaxation time τ_R of this system relative to the system *Rb*Y.

nance behavior is governed by the two frequencies ω_L/π and $\nu=1/T_0$, T_0 being the repetition time of the beam pulses (≈ 4 μs). We chose a variation of T_0 and kept B_{ext} constant at 270 G. Resonance occurs at $\omega_L T_0 = n\pi$ (n an integer). In order to increase the amplitude of the resonances we have set time gates of length 300 μs for the excitation of the isomer and time gates of length approximately $\min(\tau_R, T_{1/2})$ for the measurements of the resonances. Furthermore, the resistive heating of the targets was only applied between the time gates for measurement, leading to an undisturbed B_{ext}. These procedures allow the determination of the resonances of *Rb*Y and *RbOH*Y with a relative accuracy of about 10^{-5}; results are shown in Fig. 2.

We identify the resonance shifts observed relative to *RbOH*Y as Knight shifts, because chemical shifts[8] for ^{89}Y fall within our experimental error. The Knight shifts are determined to be $K(Rb\text{Y}) = 0.025(1)\%$ at $T=360$ K and $K(Sr\text{Y}) = 0.47(5)\%$ at $T=1080$ K. Furthermore, we found that the Larmor frequencies observed by TDPAD for liquid and solid Rb are equal within 0.1%. The relaxation times as measured by TDPAD are found to be $\tau_R(RbOH\text{Y}) \approx 90$ ms at room temperature, $\tau_R = 0.70(4)$ ms for *Sr*Y at 1180 K, and $\tau_R \gtrsim 120$ ms for Y in liquid Rb in the range 320–440 K (Ref. 5) and 90(4) ms at 740 K (see Fig. 1).

In order to estimate the magnetic part τ_m^{-1} of the relaxation rates, a possible quadrupolar contribution τ_Q^{-1} has to be taken into account. As discussed in more detail in Ref. 9, one expects a very small τ_Q^{-1} as a result of the high spin and small quadrupole moment of the 8^+ isomer. This is consistent with the long relaxation time observed for Y in RbOH. For *Sr*Y we estimate $\tau_m^{-1} \approx \tau_R^{-1}$ whereas for *Rb*Y a τ_Q^{-1} contribution to τ_R cannot be ruled out, leading to $\tau_m^{-1} \leqslant \tau_R^{-1}$.

In the following sections we analyze these magnetic hyperfine data in order to gain information about the density of s states at the Fermi level $N_s(E_F)$, which is proportional to the K_s part of the Knight shift. An extraction of K_s from K for transition ions is hampered by the fact that the d states normally give two contributions to K and to τ_m^{-1}, associated with the orbital moment (orb) and—via core polarization (cp)—with the spin of the d electrons. In our case, where spin-orbit coupling is presumably small, the quantities measured can be expressed as simple sums[10]: $\tau_m^{-1} = \tau_s^{-1} + \tau_{\text{orb}}^{-1} + \tau_{\text{cp}}^{-1}$ and $K = K_s + K_{\text{orb}} + K_{\text{cp}}$. For *Rb*Y the almost vanishing K cannot result from a cancellation of considerable contributions K_s and K_{orb} by a negative K_{cp} because these quantities are correlated with their corresponding relaxation parts by the relation that τ_i^{-1} is approximately proportional to K_i^2 (for $i=$ orb the relation holds only for d impurities in a nonmagnetic metal).[11]

Taking into account that the tensor degree of the nuclear alignment for the TDPAD experiments is found to be $\lambda = 2$ (see Ref. 6), we use the Korringa relation to obtain an upper limit $K_s(Rb\mathrm{Y}) \leq 0.04\%$. In fact, K_s is probably considerably smaller because our estimate is based on the unlikely assumption $\tau_s^{-1} = \tau_R^{-1}$ and because we disregard an enhancement factor between K_s^2 and τ_s^{-1} due to possible localization of the s electrons (see below).

This $K_s(Rb\mathrm{Y})$ value is in contrast with the findings for the SrY system where the Knight shift and magnetic relaxation are comparable to the data in the pure ^{89}Y system. As discussed in more detail in Ref. 9, we estimate the s parts to be $K_s = 0.3(1)\%$ and $\tau_s^{-1} \approx \tau_m^{-1}$ for SrY which should be compared with $K_s = 0.25\%$ and $\tau_s^{-1} = 0.83\tau_m^{-1}$ for pure ^{89}Y as analyzed by Karcher *et al.*[12] An analysis of the d contribution to K and τ_m^{-1} in the system RbY yields much less conclusive results compared with the analysis of the s contributions and will be given in Ref. 9.

The drop of K_s of RbY relative to that of SrY and pure Y is evidence for a fall of $N_s(E_\mathrm{F})$ by an order of magnitude in RbY because a change so large in the s-hyperfine fields is highly unreasonable. To the best of our knowledge, this is the first time that such an effect has been observed at a transition-metal ion.

Our findings are consistent with the idea of an s band well below the Fermi energy or with the occurrence of a pseudogap at E_F.[1,2,4] It is even possible that the 5s states are localized[1,2] on the Y ion in liquid (and solid) Rb. Evidence for localization would come from an enhancement of τ_s^{-1} relative to the Korringa rate.[1] We cannot decide upon the possibility of localization because our data yield no definite values for τ_s^{-1} and K_s. In any case the local 5s band turns out to be almost fully occupied.

The central question can now be formulated as follows: What kind of mechanism causes the sharp contrast between the s-electron behavior in SrY and RbY? Because we are dealing with systems having large positive heats of solution and rather small differences in electronegativity (EN) of the constituents, a formation of directional or ionic chemical bonds in RbY is unlikely. Such mechanisms have been proposed to explain the metal-nonmetal transition in chalcogenide alloys with large negative heats of solution[1] and in so-called ionic alloys (e.g., CsAu[3]) where charge transfer occurs as a result of the large EN difference. As another mechanism for vanishing $N_s(E_\mathrm{F})$ values, hybridization effects have been investigated[13] for Y hydrides. In view of the considerable differences in structure, ionic size, EN, and ionization energies, an analogy between the RbY and the $\mathrm{YH_2}$ systems is questionable. Still, hybridization effects as a cause for decreasing $N_s(E_\mathrm{F})$ cannot be excluded and remain to be investigated by band-structure calculations for RbY.

In the following we propose a simple line of interpretation which in our opinion is the most reasonable explanation for the anomalous behavior of RbY. We implant the Y ion into a matrix which has a much larger volume of the Wigner-Seitz cell and a very small conduction-electron density in the region of the Wigner-Seitz surface. For a qualitative discussion of the alloy formation we follow the semiempirical theory of Miedema, de Chatel, and de Boer[14] which attributes the large positive heat of solution of a hypothetical YRb alloy mainly to the extremely large difference of electron densities, ρ_out, at the boundaries of the Wigner-Seitz cells in the pure metals. After implanation of Y into the hosts, ρ_out and the difference in E_F must be smoothed out. A net charge transfer of conduction electrons from Y to Rb as a mechanism for this process seems to be rather unimportant because the EN value for Rb is smaller than for Y. Furthermore, this assumption is consistent with a nearly complete screening of the Y ion charge. Qualitatively, the alloy process can be simulated by starting with the Wigner-Seitz cells of the pure metals and expanding or compressing them until the mismatch in ρ_out vanishes. Because of the large volume of Rb one expects a large expansion of the Y cell. Consistently, such an expansion lowers $E_\mathrm{F}(\mathrm{Y})$ to about the value of $E_\mathrm{F}(\mathrm{Rb})$, if one extrapolates the behavior of E_F vs Wigner-Seitz radius of Y as calculated by Alonso and Girifalco.[15] The net result of these considerations is in accordance with the more naive picture of a large negative lattice pressure acting on the isolated Y ion in the Rb matrix.

As a consequence of the volume expansion by a factor of 2–3, the width of the conduction-electron bands at the Y site should narrow considerably. Thus, it seems to be plausible that the s band of RbY might be located well below E_F, or that E_F lies in a pseudogap between the s and d bands. An equivalent procedure for the behavior of s electrons in the Sr host leads to a much smaller volume expansion of Y. The simple and naive picture drawn above can therefore reproduce the contrasting electronic properties of the local surroundings. Furthermore, these ideas relate the microscopic electronic structure at the impurity site with the macroscopic heat-of-solution data in a satisfying manner.

It is believed that volume effects play a decisive role for metal-nonmetal transitions in liquid metals and noble gases also. Rb is among the few metals with very low critical temperatures. In some of these materials, transitions have been observed which were ascribed to a weakening of the overlap of the electron shells if the density of the metal falls below a critical value.[2] In mercury, for example, Knight-shift measurements[16] show a rather sharp decrease of $N_s(E_F)$ by a factor of 10 at the transition.

Assuming our interpretation for the *Rb*Y system to be correct, one is led to expect that *anomalous local band structures might be observed more generally for many transition metal ions if implanted into Rb or Cs metal.* We plan to test these exciting possibilities by further studies with the TDPAD and SOPAD methods combined with the powerful implantation technique following heavy-ion reactions. Electronic structure investigations in such systems are inaccessible by other means.

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