Strong Orbital Magnetism and Possible Mixed Valence in 4*d* Systems

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Tc and Ru ions in alkali-metal hosts exhibit local magnetic 4*d* moments with large orbital contributions which imply small crystal fields and spin-orbit coupling for the $4d^6$ shell of Tc in Rb. Probably we have found mixed valence for a *d* system. The results for Tc in Rb can be well reproduced by a mixture of the ionic Tc^{2+} and Tc^{1+} levels. The magnetism of Ru in Rb and Cs is consistent with a predominant $4d^7$ state along with spin fluctuations of $\sim 10^2$ K. The systems were produced and investigated by the perturbed γ-ray distribution method following heavy-ion reactions.

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Orbital effects and mixed-valence phenomena are known to play an important role for the electronic structure and magnetism of 4*f* (Refs. 1 and 2) and 5*f* systems.[3] These systems usually reflect *f* linewidths small compared to Coulomb correlation energies, which allows a treatment within a localized picture. The bulk of metallic 4*f* systems have been described in terms of ionic-type models using configurations with intact intra-atomic correlations including spin-orbit (*LS*) coupling. Essential features of this picture remain valid in unstable 4*f* systems, in particular for intermediate-valence (IV) Sm, Eu, Tm, and Yb systems, which can be described by a dynamic mixture of two ionic configurations.[1,2]

Contrary to that, the *d* electrons in metallic 3*d* systems are often assumed to be itinerant. The large 3*d* linewidth and the poor knowledge about atomic correlation energies are essential reasons for the poor knowledge about ionic-type configurations, about the number of *d* electrons and the valence, and about the role of orbital correlations in 3*d* systems. There exist only a few 3*d* systems, e.g., Co in Au,[4] Fe in Ca,[5] and Fe in alkali metals,[6] where significant orbital contributions to the magnetic moment have been identified. Orbital magnetism is often regarded as an essential test for 3*d* electron localization and for different models of 3*d* moment formation.[4-6] However, except for Fe in alkali metals[6] the orbital effects observed seem to be too weak to deduce unambiguous information about the 3*d* hybridization, ionic configurations, or crystal fields (CF). As far as we know, there is no reliable analysis of any unstable 3*d* system in terms of IV, i.e., in terms of two well defined ionic states.

In this Letter we report on the observation of orbital magnetism in 4*d* systems. The orbital contributions to the local susceptibility for extremely dilute Tc ions in Rb and for Ru ions in Rb and Cs are more than an order of magnitude higher than those found in alloying 3*d* systems and are large enough to justify an analysis based on ionic 4*d* configurations. Probably we also have found mixed valence in a *d* system. The susceptibility for Tc ions in Rb along with an analysis using a Born-Haber cycle can be well reproduced by a mixture of the two magnetic $4d^5$, Tc^{2+} and $4d^6$, Tc^{1+} states. Many of the new magnetic phenomena observed for the 4*d* shells of Tc and Ru ions in alkali metals bear a closer resemblance to unstable or IV *f* systems than to the magnetic behavior of 3*d* ions in alloying systems.

The local magnetism of the Tc and Ru systems has been investigated by the perturbed angular γ-ray distribution method which has been applied for the measurement of spin magnetic behavior of Mo ions in alkali metals before.[7] We proved the rather short-lived isomers of $\simeq$7-ns lifetime in ^{94}Tc (Ref. 8) and $\simeq$15 ns in ^{95}Ru (Ref. 9) to be suitable nuclear probes for local moment studies in metals. The systems and isomers were produced by recoil implantation following the heavy-ion reactions ^{85}Rb(^{12}C,3*n*)^{94}Tc and ^{63}Cu(^{36}Ar,3*pn*)^{95}Ru. Pulsed ^{12}C and ^{36}Ar beams with energies of 55 and 135 MeV were provided by the VICKSI accelerator at the Hahn-Meitner Institut, Berlin. Spin-rotation patterns[6,7] $R(t)$ were measured at various γ lines in an external field $B_{ext} \simeq 2$ T at temperatures in the range 20 to 300 K. Examples are shown in Fig. 1.

From the observed Larmor frequencies ω_L the local susceptibility $\beta(T)-1$ can be deduced from $\beta(T) = \hbar\omega_L/g_N\mu_N B_{ext}$. The results are shown in Figs. 2 and 3. The nuclear g_N factors of the isomeric states have been determined from the nonmagnetic systems $[\beta(T)=1]$ ^{94}Tc and ^{95}Ru in Ta to be $g_N=1.06(6)$ and $g_N=0.873(7)$,[9] respectively. A more detailed discussion of the experiments, the nuclear probes, and the hitherto unknown g_N factor of the ^{94}Tc isomer will be given elsewhere.

The results for the systems of Tc and Ru ions in alkali hosts (Figs. 1-3) can be summarized as follows: The large changes in ω_L and $\beta(T)$ are evidence for the existence of local magnetic 4*d* moments. The $\beta(T)$ values are all much larger than 1 and strongly increase with decreasing temperature which indicates predominant orbital contributions to $\beta(T)$. $\beta(T)$ does not follow a Curie-type behavior.

As will be reasoned in more detail below, such large

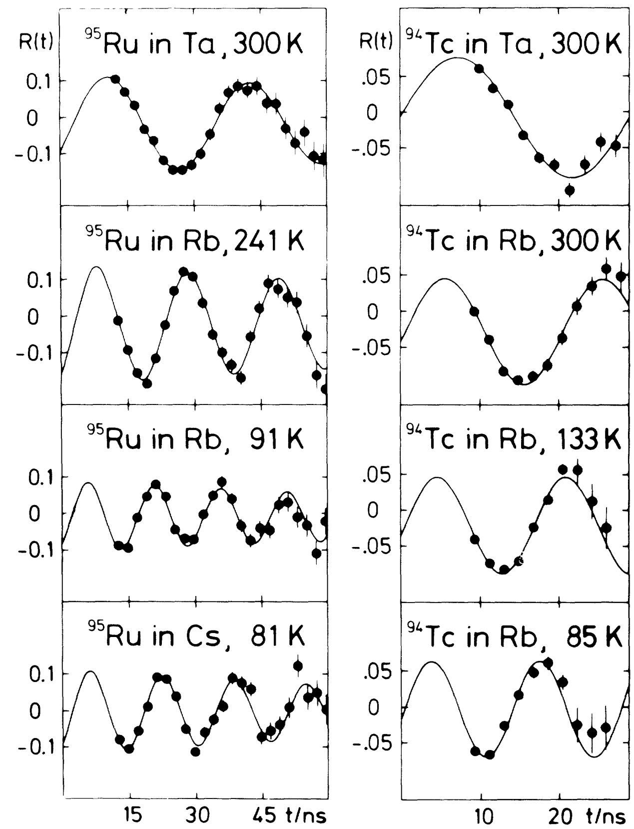

FIG. 1. Spin-rotation patterns of ^{94}Tc and ^{95}Ru ions in various hosts as a function of temperature.

orbital contributions justify a configuration-based analysis. As a first step we estimate the possible ionic states, which might contribute to $\beta(T)$, using a Born-Haber cycle. Within this cycle the energy differences[7,10,11] $\Delta E = \Delta E(\text{atom}) + \Delta E(\text{coh}) + \Delta E(\text{sol})$ between the ground state and excited states of d ions in metals are estimated under the premise that the d electrons are localized and do not contribute to the bonding. For a broader test we have applied the cycle to all nearly localized d states in Rb and/or Cs known hitherto. For the systems shown in Fig. 4 the most stable d configurations are the 1^+ and 2^+ states. The difference of cohesion energies of hypothetical 1^+ and 2^+ d metals is estimated to be $\Delta E(\text{coh}) \simeq -0.3$ eV, whereas the difference of the heats of solution of the 1^+ and 2^+ d metal cells in Rb and Cs is $\Delta E(\text{sol}) \simeq +0.6$ eV.[7] Thus as a net result the term $\Delta E(\text{sol})$ stabilizes the 1^+ states in Rb and Cs hosts compared to the separation $\Delta E(\text{atom})$ known in the free atoms (Fig. 4). The cycle correctly reproduces the observed valencies Mo^{1+} in Rb and Cs,[7] Fe^{2+} in Rb and Cs,[6] and nearly 1^+ for Ni in Cs.[12] In Fig. 4 we have not included the energy separation to the neighboring 3^+ and/or 0^+ states, since these ΔE values come out to be much larger than ΔE between 1^+ and 2^+.

As the next step we calculate $\beta(T)$ for the 1^+ and 2^+

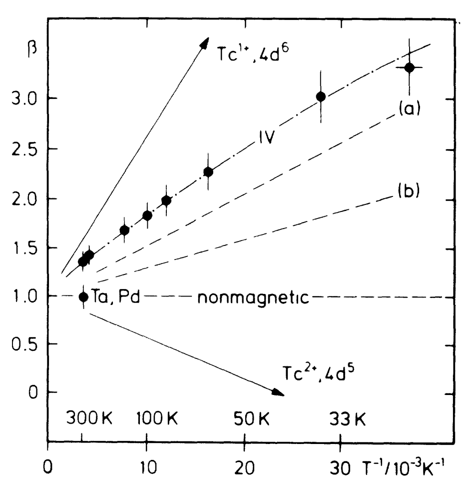

FIG. 2. Local susceptibilities of Tc ions in Rb. The lines represent $\beta(T)$ calculated for the ionic Tc^{1+} and Tc^{2+} states (solid lines), for a $4d^6$ state with decoupled L and S (line a), and for a CF-split $4d^6$, Tc^{1+} state (line b), respectively (see text).

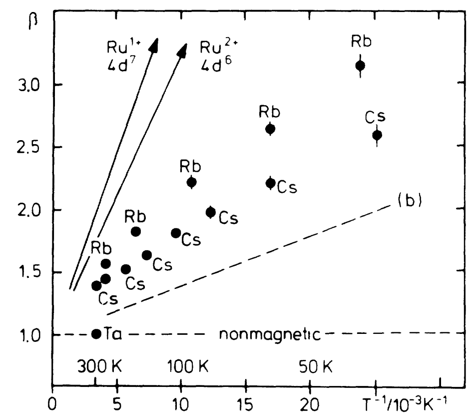

FIG. 3. $\beta(T)$ observed for Ru ions in Rb and Cs. The solid lines represent $\beta(T)$ for the ionic $4d^6$ and $4d^7$ states and line b, the CF-split $4d^7$ state of Ru^{1+} (see text).

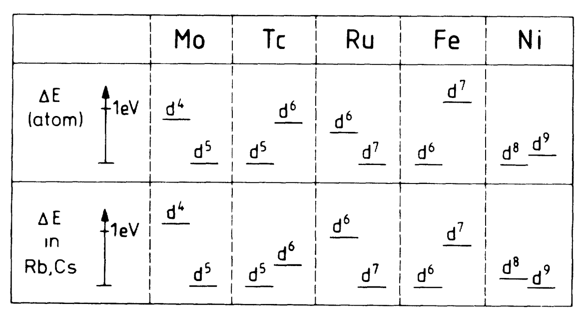

FIG. 4. Energy separation between the 2^+, d^n, and 1^+, d^{n+1} configurations for free $3d$ and $4d$ atoms and for dilute solutions of these atoms in Rb and Cs hosts as deduced from a Born-Haber cycle.

states of Tc and Ru ions in LS coupling using[6,7]

$$\beta - 1 = g_J \mu_B (J+1) B(0)/3k_B T, \quad (1)$$

where g_J is the Landé factor. In general, the magnetic hyperfine field at 0 K, $B(0)$, consists of a positive direct $4d$-shell contribution B_J which is essentially orbital, and an usually negative term B_s due to spin-polarized core s and conduction electrons. The solid lines in Figs. 2 and 3 are calculated[11] with $B(0) = +104$ T for the $J=4$, $g_J = \frac{3}{2}$ state of Tc^{1+}; $B(0) = B_s = -28$ T for the $S = \frac{5}{2}$ state of Tc^{2+}; $B(0) = +189$ T for the $J = \frac{9}{2}$, $g_J = \frac{4}{3}$ state of Ru^{1+}; and $B(0) = +131$ T for the $J=4$ state of Ru^{2+}. For an estimate of B_s we use -3 T per spin for the 1^+ states as found for Mo^{1+} in Rb (Ref. 7) and for the 2^+ states, -5.6 T per spin as known for the free $4d^5 5s^2$ Tc atom. An analysis of $\beta(T)$ with larger $|B_s|$ values would lead to more pronounced orbital effects for both the Tc and Ru systems.

Obviously the $\beta(T)$ data for Tc in Rb cannot be reproduced by the predicted $4d^5$ ground state of Tc^{2+} alone (see Figs. 2 and 4). Necessarily one has to include strong orbital components to $\beta(T)$ which most probably arise from the $4d^6$ state of Tc^{1+} lying close to the Tc^{2+} state (see Fig. 4). The observed $\beta(T)$ can be reproduced with a simple model using two ionic configurations and neglecting CF effects, which has been applied for a parametrization of the susceptibility and isomer shift in IV $4f$ systems before.[2,13] If we set $\beta - 1 = \beta'$ and start from

$$\beta'(T') = p_1(T')\beta_1'(T') + p_2(T')\beta_2'(T'), \quad (2)$$

it is sufficient to consider the most simple case of energetically degenerate levels 1 and 2—that means the linewidths are larger than the excitation energy—which leads to temperature-independent occupation probabilities given by $p_1/p_2 = (2J_1+1)/(2J_2+1)$ and $p_1 + p_2 = 1$. To include a possible influence of a spin fluctuation or Kondo temperature T_f on $\beta(T)$,[1,2,13] the temperature in Eqs. (1) and (2) is replaced[2] by $T' = T + T_f$. As shown by the line IV in Fig. 2, the observed $\beta(T)$ are well reproduced by this *Ansatz* with a small $T_f \simeq 10$ K which has a significant influence on $\beta(T)$ only at very low temperatures. Such a T_f compares roughly with $T_f \simeq 2$ K observed for Mo in Rb at 100 K (Ref. 7) and $T_f \simeq 10^2$ K estimated for Ru in Rb (see below). This simple fit to $\beta(T)$ along with the predicted positions of the 1^+ and 2^+ levels (Fig. 4) probably indicate IV for the d system Tc in Rb, i.e., a dynamic mixture of the two magnetic $S = \frac{5}{2}$, Tc^{2+} and $J=4$, Tc^{1+} states for the single Tc ion in Rb. Such an IV d system would exhibit features common to IV Sm, Eu, Tm, and Yb systems with closely lying 2^+ and 3^+ levels and small T_f values.[1,2,13] Alternative explanations of the observed $\beta(T)$ require an (unoccupied) $4d^5$ state above a $4d^6$ ground state where $\beta(T)$ of Tc^{1+} might be reduced by Kondo-type and/or CF effects. Such an alternative is more unlikely partly because an error of $\gtrsim 0.5$ eV for ΔE (Fig. 4) is hard to expect for the analyses within the cycle, especially in view of the small absolute values for all ΔE's involved.[11]

Now we turn to the question of whether LS coupling in the $4d$ shells can be inferred from the data. If one assumes the $4d^5$ state of Tc^{2+} to be the ground state, the IV picture just discussed requires a fully localized $4d^6$ shell in LS coupling to reproduce $\beta(T)$. However, LS coupling can also be inferred if one assumes that the $4d^6$ state contributes to $\beta(T)$ alone. For a hypothetical decoupled state with $L=2$ and $S=2$, the susceptibility is given by[5]

$$\beta - 1 = \{g_L \mu_B (L+1) B_L + g_s \mu_B (S+1) B_s\}/3k_B T, \quad (3)$$

which yields line a in Fig. 2. This line is well below the observed $\beta(T)$ thus indicating the presence of LS coupling for Tc in Rb. This result strongly supports the ionic-type analysis used in this paper.

Furthermore, the strong orbital effects allows us to deduce information on the role of CF effects in $4d$ systems. In analogy to analyses performed for $3d$ ions in insulators[14] and proposed for $3d$ ions in metals,[14] we assume a cubic CF of intermediate strength and calculate $\beta(T)$ for the CF-split states Γ_5, $\tilde{J} = 1$ of $4d^6$ Tc^{1+}, and Γ_4, $\tilde{J} = \frac{1}{2}$ of $4d^7$ Ru^{1+}, thus including spin-orbit effects in the CF ground states.[11] Since the calculated lines b in Figs. 2 and 3 are considerably smaller than the observed $\beta(T)$, possible CF effects are at most comparable to the LS coupling for the Tc as well as for the Ru systems under consideration. In case of the IV situation with $4d^5$ as the ground state, CF effects for $4d^6$ Tc^{1+} in Rb come out to be negligible. These results in $4d$ systems along with the undetectable small CF for Fe in alkali-metal hosts[6] suggests a critical view on assumptions that CF splittings of $3d$ and $4d$ ions in metals are $\simeq 1$ eV and thus unobservably large. Especially it seems to be impossible to extrapolate CF effects known for d ions in insulators to the metallic situation because of screening and (anti) shielding of electric multipole moments by conduction electrons.

$\beta(T)$ observed for Ru in Rb and Cs is smaller compared to both the stable Ru^{1+} and Ru^{2+} behaviors (Fig. 3). If we neglect CF effects, such a reduction of $\beta(T)$ has to be interpreted as being predominantly caused by large spin fluctuations which also holds for the case of a possible mixture of the 1^+ and 2^+ states [see Fig. 3 and Eq. (2)]. For simplicity, we assume that the predicted Ru^{1+} ground state (Fig. 4) contributes to $\beta(T)$ alone and use a Curie-Weiss law $\beta - 1 = C/(T + T_f)$ as a rough approximation to the observed $\beta(T)$ which yields T_f values of a few 10^2 K for Ru in Rb and Cs. This analysis in terms of $4d$ instabilities predominated by large spin fluctuations is strongly supported by the nuclear spin relaxation observed for Ru in Rb and Cs. These data allow us to estimate[7] a lower limit of the $4d$ spin rate of $\tau_J^{-1} \simeq 7 \times 10^{12}$ s^{-1}, which corresponds to $T_f \gtrsim 50$ K for Ru in Rb and Cs. The observed $\beta(T)$ for the Ru systems and the interpretation suggested here bears resemblance to strongly unstable $4f$ systems like Pr in Pt and Nd in Ta (Ref. 15) in which $\beta(T)$ has been observed to be reduced compared to both the magnetic 3^+ and 4^+ ionic states and which has been interpreted as large $4f$ spin fluctuations.[13,15]

In summary, the findings of large orbital effects and small crystal fields imply a very small interaction of the $4d$ shells of Tc and Ru with the conduction electrons and/or ligands in alkali-metal hosts which mainly originates from the large cell volumes of the hosts and the s-like character of the host conduction electrons. We have probably found dynamic mixed-valence behavior for the 1^+ and 2^+ levels of Tc ions in Rb. The magnetic response of Ru ions in Rb and Cs seems to be predominated by spin fluctuations of $\simeq 10^2$ K. Large orbital effects, small crystal fields, ionic ground states, mixed valence, and measurable influences of spin fluctuations on $\beta(T)$—these phenomena exhibit basic features common with stable and unstable $4f$ and $5f$ systems but partly reflect qualitative differences from the magnetism of $3d$ ions in Cu, Ag, Au, and in d-metal hosts.

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[1]J. M. Lawrence, P. S. Riseborough, and R. D. Parks, Rep. Prog. Phys. **44**, 1 (1981).

[2]D. Wohlleben, in *Valence Fluctuations in Solids,* edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 1.

[3]G. H. Lander, in *Moment Formation in Solids,* edited by W. J. L. Buyers (Plenum, New York, 1984), p. 207.

[4]R. Dupree, R. E. Walstedt, and W. W. Warren, Jr., Phys. Rev. Lett. **38**, 612 (1977).

[5]M. H. Rafailovich, D. Dafni, H. E. Mahnke, and G. D. Sprouse, Phys. Rev. Lett. **50**, 1001 (1983).

[6]D. Riegel, H. J. Barth, L. Büermann, H. Haas, and Ch. Stenzel, Phys. Rev. Lett. **57**, 388 (1986).

[7]D. Riegel, K. D. Gross, and M. Luszik-Bhadra, Phys. Rev. Lett. **59**, 1244 (1987).

[8]I. Y. Lee, N. R. Johnson, F. K. McGovern, G. R. Young, M. W. Guidry, and S. W. Yates, Phys. Rev. C **24**, 293 (1981).

[9]P. Chowdhury, B. A. Brown, U. Garg, R. D. McKeown, T. P. Sjoreen, and D. B. Fossan, Phys. Rev. C **32**, 1238 (1985). Lifetime and g_N values are averages over two nuclear isomers in ^{95}Ru (H. Grawe, private communication).

[10]M. Martensson, R. Nyholm, H. Calén, J. Hedman, and B. Johansson, Phys. Rev. B **24**, 1725 (1981).

[11]A more detailed description of the cycle and of $\beta(T)$ for localized d states including possible CF effects on $\beta(T)$ will be given in a forthcoming paper.

[12]H. Haas, Ch. Stenzel, and D. Riegel, Annual Report of Bereich P, Hahn-Meitner Institute, Berlin, 1985 (unpublished), p. 93.

[13]M. Luszik-Bhadra, H. J. Barth, H. J. Brocksch, G. Netz, D. Riegel, and H. H. Bertschat, Phys. Rev. Lett. **47**, 871 (1981); D. Riegel, J. Magn. Magn. Mater. **52**, 96 (1985).

[14]A. Abragam and B. Bleaney, in *Electron Paramagnetic Resonance in Transition Ions* (Clarendon, Oxford, 1970); L. L. Hirst, Z. Phys. **241**, 9 (1971).

[15]L. Büermann, H. J. Barth, K. H. Biedermann, M. Luszik-Bhadra, and D. Riegel, Phys. Rev. Lett. **56**, 492 (1986).