Observation of a Local Magnetic 4*d* Moment and Its Spin Dynamics

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By application of the perturbed γ-ray distribution method following heavy-ion reactions, we have found an experimental method of producing and investigating strong local 4*d* magnetism in metals. Mo ions recoil implanted into alkali metals show a large local moment and an extremely small 4*d* spin-relaxation rate. The data along with an analysis using a Born-Haber cycle are consistent with a localized $4d^5$ shell behavior for isolated Mo ions in Rb and Cs.

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The formation of local magnetic moments and the problem of *d*- and *f*-electron localization in dilute and concentrated metallic systems has been extensively investigated for atoms of the 3*d*, 4*f*, and 5*f* transition groups. Much less experimental evidence is presently available about the tendencies towards magnetic or localized behavior of 4*d* atoms in metals. Weak-itinerant magnetism has been observed in $ZrZn_2$.[1] Besides, the enhanced susceptibilities found in Pd metal,[2] in Au-Pd-Au sandwiches,[2] and in concentrated and dilute Rh systems[3] might be regarded as signals of incipient magnetism in 4*d* systems.

Compared to 3*d* systems, the hybridization of 4*d* electrons with conduction electrons (CE) and/or ligands is much larger in 4*d* systems, mainly due to the larger ratio of 4*d*-shell volume to the Wigner-Seitz volume. This is supported by, e.g., cluster calculations of 3*d* and 4*d* impurities in Cu,[4] and by the results from high-energy-electron spectroscopies.[5] The 4*d* linewidth has been analyzed to be about 0.6 eV for Pd in noble metals[5] and can be expected to be larger in nearly all other Pd-host systems and for systems containing other 4*d* ions.[4,5] These large 4*d* linewidths seem to be the reason that atomic correlations and local magnetism are hard to detect in 4*d* systems.

In this paper we describe an experimental method of producing and investigating strong local magnetism of 4*d* ions in metallic hosts. As a 4*d* ion we have used Mo as a test case under the speculative assumption that a possible magnetic 4*d* moment is more stable for the 4*d* ion with a half-filled shell compared with the 4*d* ions at the ends of the series, in analogy to the rather systematic trends known for local-moment formation of 3*d* ions in metals. We have implanted the Mo ions into alkali-metal hosts, since the 4*d*-CE hybridization might be small in Rb and Cs hosts, because of the large differences of the volumes of the metallic cells of 4*d* ions compared to Rb and Cs.[6] We have observed strong local 4*d* moments with a Curie-type temperature dependence of the local susceptibility for the systems Mo in Rb and Cs. In addition, it has been possible to observe the 4*d* spin dynamics. The perhaps most surprising message of this work is the finding of extremely small 4*d* spin rates for Mo in Rb and Cs, from which the Mo moment can be classified to be one of the most stable magnetic moments known in metallic *d* systems.

The nonalloying Mo–alkali-metal systems were produced by recoil implantation following heavy-ion reactions. The static and dynamic magnetic responses of the extremely dilute Mo ions were measured by the time-differential perturbed γ-ray distribution (TDPAD) method.[6] Table I gives a survey of the Mo isomers, which served as nuclear probes to detect the magnetic hyperfine interaction of the Mo ions. The experiments were performed at the VICKSI accelerator at the Hahn-Meitner-Institut, Berlin, using pulsed ^{12}C, ^{17}O, and ^{36}Ar beams with energies of 55, 60, and 135 MeV, respectively. The target assembly was mounted to the Cu cold finger of a liquid-He cryostat, which allowed a variation of temperature between 10 and 300 K.

Spin-rotation patterns, $R(t)$,[6] were measured with various γ lines in an external field B_{ext} around 2 T (see Fig. 1). From $R(t)$, the Larmor frequency ω_L and the spin-relaxation time τ_N can be extracted. In all spectra only one frequency with high amplitude is observed, which supports the assumption that the *d* ions come to rest predominantly at a unique lattice site, probably at a substitutional site.[9] The large changes in ω_L as a function of temperature and host are caused by the existence of a local Mo moment in Rb and Cs. From $\omega_L = \hbar^{-1} \times \mu_N g_N B_{\text{ext}} \beta$ the local susceptibility $\beta(T) - 1$ can be deduced; the results are displayed in Fig. 2. $\beta(T) \equiv 1$ indicates nonmagnetic behavior. For both Mo in Rb and in Cs, $\beta(T)$ nicely follows a Curie-type behavior in its simplest form: $\beta - 1 \propto \text{const}/T$.

The initial analysis of β and of the 4*d* spin dynamics

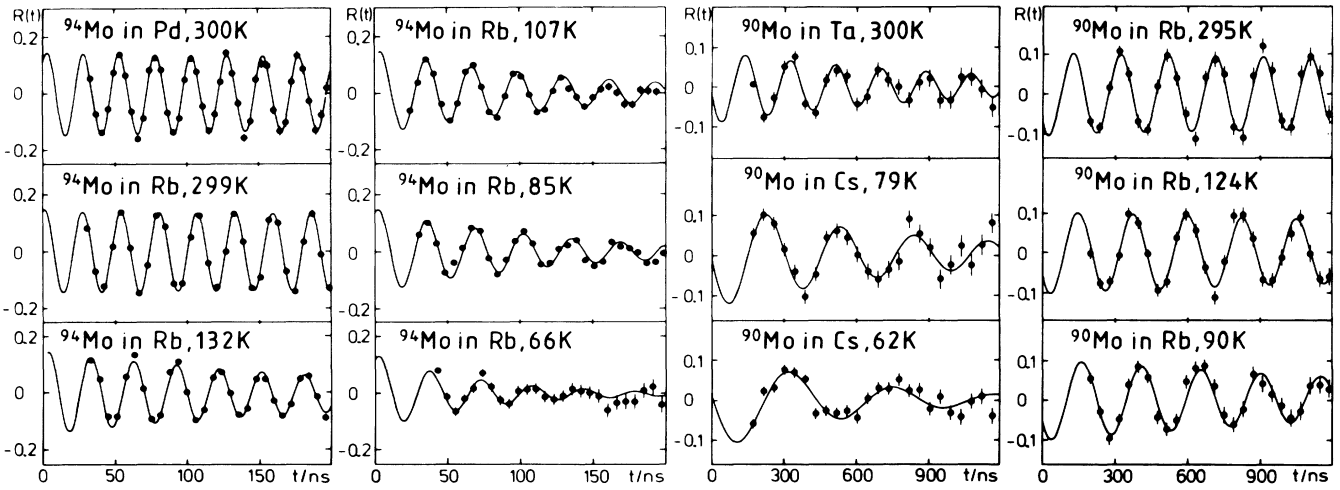

FIG. 1. Spin rotation patterns of Mo in several metal hosts. The temperature- and host-dependent frequencies reflect the existence of a local Mo moment in Rb and Cs.

will be carried out under the assumption that the magnetic response of Mo in Rb and Cs is dominated by a half-filled $4d$ shell with an effective spin $S=\frac{5}{2}$; arguments for this will be given below. With use of[6]

$$\beta-1=g_s\mu_B(S+1)B(0)/(3k_BT), \quad (1)$$

it is then possible to deduce the magnetic hyperfine fields to be $B(0)=-20$ T for Mo in Cs and $B(0)=-13$ T for Mo in Rb. The fits are indicated in Fig. 2 by the dashed lines. The negative $B(0)$ values are consistent with the predominance of spin magnetism and are regarded to arise from spin polarization of the core s electrons and conduction electrons. $B(0)$ compares roughly with values known for Mn and Gd ions in metals. At present, $B(0)$ values for $4d$ ions in metals are hard to estimate, partly because of the theoretical prediction of a very large contribution of +139 T from core polarized $5s^2$ for Mo atoms.[10] The difference between the $B(0)$ values of Mo in Cs and Rb (Fig. 2) might also be related to the crucial role of outer s electrons. Details will be discussed elsewhere.

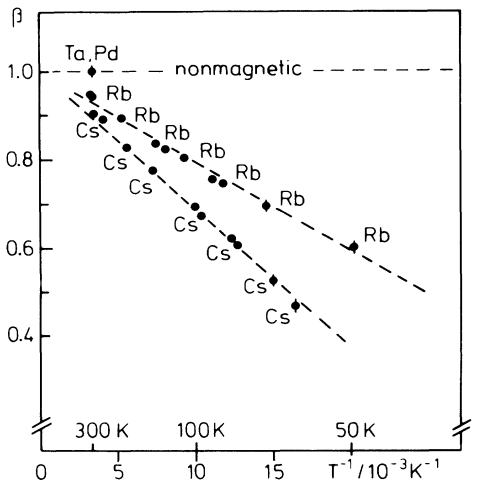

FIG. 2. Local susceptibilities of isolated Mo ions in Rb and Cs. The Curie-type behavior is represented by the dashed lines.

As far as we know, no experimental evidence is presently available about the spin dynamics of $4d$ atoms in metals. We have performed a series of TDPAD experiments in order to disentangle magnetic, $\tau_N^{-1}(m)$, and quadrupolar contributions to the total rates observed. Since the q_N factors of the isomers in ^{92,94}Mo and ^{90}Mo are quite different and the quadrupolar moments are known to be nearly equal (Table I), the magnetic rates can be determined unambiguously by measuring τ_N^{-1} for these isomers in the same host. The derived $\tau_N(m)$ values are shown in Fig. 3(a).

For stable systems, the relation between the nuclear rate $\tau_N^{-1}(m)$ and the $4d$ spin-relaxation rate, τ_J^{-1}, is given by[11]

$$\tau_N^{-1}(m)=2(\mu_N/\hbar)^2S^{-1}(S+1)g_N^2B^2(0)\tau_J. \quad (2)$$

TABLE I. Half-lives and nuclear moments of the 8^+ states in Mo isotopes and some nuclear reactions used to produce the systems.

Isotope	$T_{1/2}$ (ns)	g_N	$\lvert Q\rvert$ (e fm^2)	Reaction
^{90}Mo	1100	−0.174[a]	58[b]	^{61}Ni(^{36}Ar,$\alpha 2pn$)
^{92}Mo	214	1.41[a]	34[b]	^{78}Se(^{17}O,3n)
^{94}Mo	98	1.31	47[b]	^{80}Se(^{17}O,3n)
				^{85}Rb(^{12}C,$p2n$)

[a]Reference 7. [b]Reference 8.

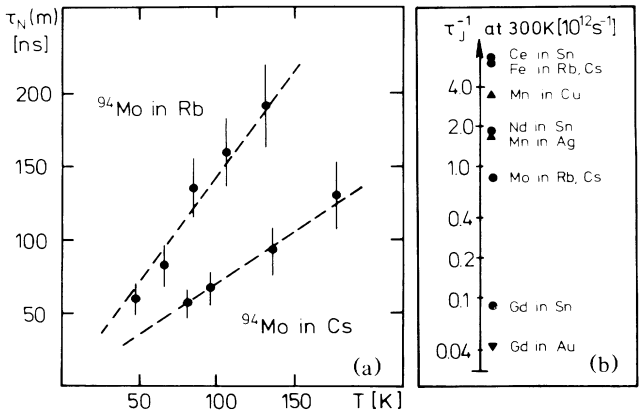

FIG. 3. Nuclear magnetic relaxation times for Mo in Rb and Cs. (a) Dashed line corresponds to the Korringa law, $\tau_N(m) \propto \tau_J^{-1} \propto T$. (b) Comparison of the spin rates in selected systems as observed by ESR (filled inverted triangles), n scattering (filled triangles), and TDPAD (filled circles), all are extrapolated to 300 K.

We would like to note the following results: (a) Since $\tau_N(m) \propto \tau_J^{-1}$, the $4d$ spin rates for Mo in Rb and Cs follows a Korringa-type behavior $\tau_J^{-1} \propto T$ [Fig. 3(a)]. (b) By use of Eq. (2) with S assumed to be $\frac{5}{2}$ and the $B(0)$ values given above, it follows that the τ_J^{-1} rates for Mo in Rb and Cs are almost equal; the rates observed at 100 K are $\tau_J^{-1} = 0.27 \times 10^{12}$ s^{-1}, which correspond to a spin linewidth of $\simeq 0.2$ meV. (c) Starting from the Korringa relation $\tau_J^{-1} = 4\pi\hbar^{-1}\{N(E_F)J_{mix}\}^2 k_B T$, where J_{mix} is the effective mixing exchange integral,[11] the exchange coupling $|N(E_F)J_{mix}|$ can be deduced to be 0.04.

The values thus derived for the τ_J^{-1} rates and exchange couplings are extremely small. This can be seen by inspection of Fig. 3(b), where the $4d$ rates are compared with the rates observed for selected $3d$ and $4f$ ions in s metal hosts and in Sn. The rates observed for Mo in Rb and Cs are smaller than the rates of the localized $3d^6$ shell for Fe in Rb and Cs[6] and are smaller than the rates for Mn in Cu[12] and Ag.[12] The $4d$ rates are also smaller than τ_J^{-1} known for some dilute Ce, Pr, and Nd systems[11] and exceed the rates for Gd in Au[13] and Sn[11] by only a factor of about 10 [Fig. 3(b)]. Mn in Ag and Gd systems are often regarded to be the prototypes of the most stable $3d$ and $4f$ systems,[14] respectively. With the rough approach that the total density is given by $N(E_F)$ of the host, $|J_{mix}|$ is found to be 0.05 eV for Mo in Cs, which is about ten times smaller than $|J_{mix}|$ for Mn in Ag.

The Curie-type $\beta(T)$, the Korringa-type $\tau_J^{-1}(T)$, and in particular the small spin linewidth—these properties are characteristic of a stable $4d$ moment where atomic correlations are larger than the $4d$ linewidth. In order to get insight into the character of a possible localized $4d$ ground state, we used a Born-Haber cycle to estimate the energy difference $\Delta E = \Delta E(\text{atom}) + \Delta E(\text{coh}) + \Delta E(\text{sol})$[15] between the $4d$ ground state and excited states of Mo in Rb and Cs. The analysis is performed under the premise of localized $4d$ states; $4d$-CE hybridization is neglected. In the Mo atom, the separation between the $4d^5 5s$ ground state and the $4d^4 5s^2$ state is known to be $\Delta E(\text{atom}) = 0.7$ eV, after averaging over the terms $^7S_3$ and $^5S_2$.

The cohesive energies $\Delta E(\text{coh})$ and the heats of solution, $\Delta E(\text{sol})$, of the new kind of ions Mo^{1+} and Mo^{2+} in alkali metals are not available, but these properties for the alkali-like Mo^{1+} and the alkaline-earth-like Mo^{2+} can be reasonably approximated by values given for Na^{1+} and Mg^{2+} (and Ca^{2+}, Zn^{2+}), respectively.[16] This procedure results in $\Delta E(\text{coh}) \simeq -0.4$ eV and $\Delta E(\text{sol}) \simeq 0.7$ eV for Mo in Cs.[16] Thus, the cycle yields that the 1^+, $4d^5$ configuration is the ground state. The next excited 2^+, $4d^4$ state is separated by $\Delta E \simeq 1.0$ eV and $\Delta E \simeq 0.9$ eV for Mo in Cs and Rb, respectively. Even larger $\Delta E \simeq 4$ eV are estimated for the differences between the 1^+ and 0^+, $4d^6$ states.

We are now in a position to put together the arguments for the assumption of a half-filled $4d^5$ configuration with S close to $\frac{5}{2}$. Under the premise that the $4d$ electrons of Mo in Rb and Cs can be described by localized ionic states, the Born-Haber cycle yields a high stability of the $4d^5$ ground state. The large ΔE values are one of the reasons that we have omitted a discussion of β and τ_J^{-1} in terms of ionic $4d^4$ and $4d^6$ configurations, where orbital contributions might be quenched by crystal-field effects. The assumption of a stable $4d^5$ configuration is strongly supported by the finding of large orbital contributions for the neighboring ions Tc and Ru in Rb and Cs hosts, which imply local moments of more than half of the ionic $4d^6$ and $4d^7$ values, respectively.[16] Since orbital moments are often assumed to be quenched more rapidly compared with spin moments, it is unlikely that the spin of Mo in Rb and Cs is less than $\frac{3}{2}$. More likely, the spin is close to $\frac{5}{2}$, which in addition is strongly supported by the small τ_J^{-1} rates observed. These rates point to a small $4d$-CE hybridization and are far too small to cause a reduction of the local moment by Kondo-like effects. This argument remains valid for the case $S \simeq \frac{3}{2}$: According to Eqs. (1) and (2), $B(0)$ increases by a factor of 1.5, and the τ_J^{-1} rates increase by a factor of 2.3. Since nearly all of the essential results of this work do not depend on the variation of S, $B(0)$, and τ_J^{-1} within these ranges, we have analyzed the data by using the probable value $S = \frac{5}{2}$.

What are the reasons for the drastically enhanced magnetism observed? For a qualitative discussion, we use the proportionality[17] $|N(E_F)J_{mix}| \propto N(E_F)V_{mix}^2/|U|$ as inverse measure for moment stability and localization. As the leading mechanism we suggest a drastic decrease of the matrix element for hybridization V_{mix}^2. The $4d$-s hybridization should approximately scale with one over the host cell volume squared, which results in a

decrease of V_{mix}^2 by more than an order of magnitude compared with alloying Mo systems. This estimate is consistent with the much smaller $|J_{\mathrm{mix}}|$ values for Mo in Rb and Cs, compared with Mn in noble metals as analyzed from the rates observed. The role of $N(E_F)$ of the host seems to be less decisive, since there are almost no $4d$ moment in insulators, and since $N(E_F)$ for Cs is about 5 times larger compared with $N(E_F)$ of the noble metals, where neither experimental nor theoretical[4] indications for $4d$ moment formation exist. Also decisive might be a large atomic correlation energy $|U|$. Large $|U|$ values are often attributed to ions with half-filled shells, e.g., for Mn and Cr in metals. For an estimate, we assume U^{-1} to be the sum of the inverse ΔE values (compare Ref. 17), calculated above for the excitation energies between the $4d^5$ state and the neighboring $4d$ states. This results in $|U| \simeq 1$ eV for Mo in Rb and Cs.

Thus, the strong $4d$ moment and the extremely small exchange coupling observed for Mo and Rb and Cs might be interpreted in terms of a small ratio of the $4d$ linewidth over the intra-atomic correlation energies. It appears clearly possible to us that the $4d^5$ shell of Mo in Rb and Cs is localized, described by $L=0$, $S=\frac{5}{2}$, in analogy to the $3d$-shell localization observed for Fe ions in K, Rb, and Cs.[6]

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