Experimental and Theoretical Study of the Magnetism and Local Lattice Structure of d Ions in Alkali-Metal Hosts

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The local susceptibility of isolated Mo ions in Na is observed to be consistent with a localized, magnetic $4d^5$ state of Mo¹⁺. Size, valence, and bonds of such Mo¹⁺ cells are similar to the host Na¹⁺ cells. These features allow study of 4d magnetism by local-spin-density calculations using substitutional Mo ions in Na. We calculate an effective moment of more than $5\mu_B$ for Mo in Na. In the larger hosts K, Rb, and Cs, we propose unusual large lattice contractions around d ions with localized d states, up to 22% for the extreme case of Fe²⁺ in Cs. This results from impurity-host bond strengths larger than those between host atoms along with the very large compressibilities of K, Rb, and Cs.

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In recent works¹ an experimental way of producing and investigating nearly localized 3d and 4d states in alkali hosts has been reported. 3d and 4d ions in the large-volume alkali metals Rb and Cs reflect the phenomena of strong local magnetism, large orbital contributions, extremely small spin rates, well-defined ionic configurations, mixed valence, and crystal fields smaller than the spin-orbit coupling (LS).¹⁻⁵ These findings have upset long-standing ideas and conceptions about the nature and the strength of the interaction of d orbitals with conduction electrons and ligands in metal hosts. The results revealed a close resemblance of the 3d and 4d magnetism in alkali hosts to the behavior known for 4f (and 5f) systems^{1,4,5} and also layed a new foundation for the interpretation of the magnetism and electronic structure of Fe ions in metal hosts.⁵

For an improved qualitative and quantitative insight into this important class of magnetic systems, further investigations on the behavior of metallic 3d and 4d ions with localized d shells and their interaction with the alkali hosts are necessary. In particular, in the large Rb and Cs lattices the present knowledge about the lattice site and local lattice structure is very poor but important for a basic understanding of the mechanism of d localization in alkali-metal hosts and indispensable for any trial of a quantitative theoretical investigation.

In this Letter we report on the finding and investigation of a system, Mo in Na, which exhibits strong 4dmagnetism and simultaneously allows a reasonable estimate of lattice site and local lattice structure. Size and valence of a metallic Mo¹⁺ cell are similar to the host Na¹⁺ cell and justify the assumption of substitutional occupancy and small lattice relaxation of the surrounding host atoms. For this simple system, we have investigated the electronic structure by *ab initio* local-spindensity functional calculations and found theoretical predictions for the magnetism of Mo in Na in agreement with the experimental results. Furthermore, we present considerations on the lattice site and local lattice structure for the widely investigated cases of undersized 3d and 4d ions in the large-volume alkali-metal hosts K, Rb, and Cs. For such systems, we propose unusual large lattice contractions around the d ion which can be as large as 22% for the extreme case of Fe²⁺ ions in Cs. The new picture for the local lattice structure is compared to the experimental trends for localization and d spin-fluctuation rates of 3d and 4d ions in alkali-metal hosts.

The local magnetism of Mo in Na has been investigated using the time differential perturbed γ -ray distribution method. We used the $I^{\pi}=8^+$, $T_{1/2}=98$ ns, g_N = 1.31 isomer of ⁹⁴Mo as a nuclear probe for the detection of the static and dynamic magnetic response of the Mo ions. The systems and isomers were produced by recoil implantation following the heavy-ion reaction ${}^{80}\text{Se}({}^{17}\text{O},3n){}^{94}\text{Mo}$. The experiments were performed at the VICKSI accelerator at the Hahn-Meitner-Institut, Berlin, using a pulsed ${}^{17}\text{O}$ beam of energy 50 MeV. A detailed description of the experimental aspects can be found in Refs. 1 and 3.

Figure 1 shows spin rotation patterns, R(t), for ⁹⁴Mo in metal hosts, as measured at temperatures between 60 and 300 K in an external field B_{ext} around 2 T. From R(t), the Larmor frequency ω_L and the nuclear spinrelaxation time τ_N can be deduced. In all spectra only one frequency has been observed which supports the assumption that the Mo ions, contributing to R(t), come to rest predominantly at a unique lattice site. From the Larmor frequencies $\omega_L(T) = \hbar^{-1}g_N\mu_N B_{ext}\beta(T)$ the local susceptibility $\beta(T) - 1$ can be extracted.¹ The results for Mo ions in Na are displayed in Fig. 2. $\beta(T) \equiv 1$ indicates nonmagnetic behavior, as found, e.g., for Mo in Pd and Ta. The β values observed for Mo in Na follow a Curie-type behavior and nearly coincide with the earlier



FIG. 1. Spin rotation patterns of ⁹⁴Mo in several hosts at various temperatures.

results for Mo in Cs (Fig. 2). Following the discussion for Mo in Cs,³ the magnetic response of Mo in Na is consistent with a localized $4d^5$ state with $S = \frac{5}{2}$ of Mo¹⁺. Using the relation^{1,3} $\beta - 1 = g_s \mu_B (S+1)B(0)/$ $3k_BT$ with $S = \frac{5}{2}$ one extracts from the slope of the β line in Fig. 2 the magnetic hyperfine field to be B(0) = -20 T.

The R(t) spectra also yield information on the spin dynamics of Mo ions in Na. In contrast to the results for Mo in Rb and Cs, no nuclear spin-relaxation τ_N could be detected for ⁹⁴Mo in Na over the whole temperature range between 60 and 300 K. To demonstrate this different damping behavior we have included in Fig. 1 a R(t) spectrum measured for ⁹⁴Mo in Cs at 90 K. The data yield a lower estimate for the 4d spin-relaxation rate of $\tau_J^{-1} \ge 2 \times 10^{12} \text{ s}^{-1}$ which is more than 8 times larger than τ_J^{-1} deduced for Mo in Rb and Cs at 100 K³ and indicate an enhanced spin fluctuation or Kondo temperature T_K of the Mo moment in Na. An upper limit for T_K can be deduced by comparing the observed $\beta(T)$ with the Curie-Weiss law $\beta - 1 = const/(T + T_K)$ which yields T_K smaller than 50 K for Mo in Na. The slightly reduced β for Mo in Na compared to Mo in Cs (Fig. 2) might be caused by a spin-fluctuation rate with T_K of the order 10 K.

In addition to the observed magnetic response for Mo in Na, there are further arguments in favor of the important assumption of a localized $4d^5$ state of Mo¹⁺ ions in Na. The interpretation of the magnetism for Mo in Na in terms of an ionic configuration is strongly supported by the fact that the observed large orbital contributions for the neighboring Tc and Ru ions in alkali-metal hosts⁴ are clearly analyzed within an ionic picture. An analysis using a Born-Haber cycle^{3,4} also leads to a 1⁺,4d⁵ ionic



FIG. 2. Local susceptibilities of isolated Mo ions in Na, Ta, Pd, and Cs. The straight line represents the Curie-type behavior for Mo in Cs taken from Ref. 3.

ground state for Mo in Na with excitation energies of 0.8 eV and ~ 4 eV to the neighboring $2^+, 4d^4$ and $0^+, 4d^6$ configurations, respectively. These combined results therefore strongly support a magnetic, ionic-type $4d^5$ configuration of Mo in Na.

Localized Mo and more generally 3d and 4d cells with (nearly) localized d electrons and integral valences 1^+ or 2⁺ represent a hitherto unknown class of metallic transition ions with largely different physical and chemical properties compared to the bulk materials where the delectrons strongly contribute to the bonding. For the dion-alkali-metal host systems under consideration, the delectrons are (nearly) nonbonding and the localized 1⁺ and 2^+ d cells chemically resemble alkali and earth alkaline cells, respectively. Furthermore, the nonbonding character of the d electrons is expected to lead to bond lengths and metallic radii in a hypothetical 1^+ and $2^+ d$ metal which are considerably larger than in the transition metals. This effect of enlarged metallic radii is particularly important for an estimate of the lattice site of localized d ions in alkali metals and will be now discussed in more detail.

Figure 3 shows the metallic single-bond radii R_1 for the first and second long period of elements. The R_1 values are related to the more familiar metallic radii R_{12} for ligancy 12 by a semiempirical equation given by Pauling.⁶ By definition of R_1 the effect of different ligand numbers and symmetries on the bond length in various metallic elements are averaged out, so that R_1 allows a comparison of the dependence of metallic radii on the character of the conduction electrons, i.e., depending on the strength of s, p, and d contributions to the bonding. The small R_1 parameters of the transition metals (Fig. 3) mainly result from the large-d contributions to the bonding, giving rise to the formation of broad dbands and a strong contraction of the systems. Under the premise of localized d states, the d contributions vanish and the bondings show predominant s or sp character. Assuming pure sp bonding along the transition metal rows, the R_1 parameters have been estimated by Paul-



FIG. 3. Metallic single-bond radii R_1 for Na, Mg, and for the 3d and 4d row of elements. The straight solid and dashed lines represent the estimated R_1 parameters for localized $2^+, d^n$ and $1^+, d^{n+1}$ ions, respectively.

ing⁶ to follow the straight lines in Fig. 3. These R_1 values give a measure of the metallic single-bond radii of localized 2^+ , d^n and 1^+ , d^{n+1} cells, respectively (Fig. 3). The drastic increase of the metallic radius leads to a volume of a Mo¹⁺ cell which is almost 4 times larger than of a Mo cell in Mo metal and even somewhat larger than of a Na cell. In this context we note that the R_1 values given in Fig. 3 for Mo¹⁺, Mo²⁺, Fe¹⁺, and Fe²⁺ should be regarded as maximum estimates since increased p admixtures or possible small d admixtures would reduce R_1 and R_{12} . We also note that another decrease of the bond length for Mo and Fe in alkali metals is expected to arise from the higher electronegativity of the d cells.⁶ Thus it is reasonable to assume that Mo ions occupy substitutional lattice sites in Na with only moderate lattice relaxations.

There are quite different size relations between the dion and alkali host atoms in the widely investigated cases of d ions in Rb and Cs.¹⁻⁵ Here d ions with localized d states are undersized and under the premise of a rigid lattice of alkali ions one rather expects interstitial occupancies. However, we feel that in these cases the usual assumption of an almost rigid lattice is not justified and instead propose a picture which is governed by strong inward relaxations of the Rb or Cs host ions around the 1^+ and 2^+ d cells. We suppose that Mo¹⁺ and Fe²⁺ ions form much stronger metallic bonds to their neighboring alkali ions than the Rb and Cs ions to each other. The higher bond strengths are expected from smaller metallic radii and higher electronegativities⁶ of the dions compared to K, Rb, and Cs and along with the extraordinarily high compressibilities⁷ of K, Rb, and Cs these strong attractive forces should lead to a drastic lattice contraction in the vicinity of the d ion. According to the higher bond number, the lattice contraction around Fe^{2+} can be expected to be considerably stronger compared to Mo¹⁺ in the same host. Applying Pauling's concept of bond lengths to an impurity atom in a metal,⁶ we have calculated the bond lengths to be 4.94 Å for Mo^{1+} in Cs and 4.22 Å for Fe^{2+} in Cs. By using 5.42 Å for the Cs host, this corresponds to lattice relaxations of the nearest Cs neighbor of $\sim 9\%$ for Mo¹⁺ and $\sim 22\%$ for Fe²⁺. Analogously one finds lattice relaxations of ~6% for Mo¹⁺ in Rb and of ~18% and ~20% for Fe^{2+} in K and Rb, respectively.

The proposed picture is supported by the magnetic response observed for Fe and Mo in alkali metals which reflects (nearly) 2⁺, 3d⁶ states for Fe in Li, Na, K, Rb, $Cs^{2,5}$ and $1^+, 4d^5$ states for Mo in Na, Rb, and Cs. A finer scale for the interaction of the d states with the host conduction electrons can be deduced from the d spin rates τ_{I}^{-1} measured for the various systems. It has been suggested $^{1-3,5}$ that the matrix element for s-d hybridization is the leading term for these spin rates.⁸ The s-dcan be roughly scaled by the atomic s-wave density of the neighboring alkali ions at the *d*-ion site. In our picture for the local lattice structure, the atomic distances are given by the bond lengths calculated above and nearly constant hybridization strengths result for Fe in K, Rb, and Cs and for Mo in Rb and Cs, whereas the s-doverlap increases in Na and even more in Li. These trends of hybridization strengths compare favorably to the measured τ_J^{-1} rates which are constant for Fe in K, Rb, and Cs² and for Mo in Rb and Cs³ but strongly enhanced for Fe in Na and Li^{2,5} and for Mo in Na (Fig. 1) and Li. This nice consistence between the d spin rates and the estimated s-d overlap, which naturally follows within our assumed local lattices structure, is hardly explainable under the premise of rigid alkali lattices and assuming substitutional sites for Fe and Mo in Li and Na but interstitial sites for Fe and Mo in Rb and Cs.

The above results indicate that Mo in Na is a good candidate for studying the 4d magnetism and electronic structure by means of local-spin-density functional calculations.⁹ To our knowledge this is the first application of an *ab initio* method to calculate the magnetic properties of a *d* ion in a simple *s* metal host. We also have chosen the example Mo in Na, since for the $4d^5$ configuration the neglect of orbital correlations within the calculations should be more tolerable compared to the systems Fe, Tc, and Ru in alkali-metal hosts, which exhibit large orbital moments. The Mo¹⁺ ions are assumed to be on substitutional sites. From our experience we expect that the calculated magnetic moment does not change much by including the here neglected (small) lattice relaxations.¹⁰

The calculations are based on the muffin-tin Green'sfunction method to solve the single-particle Kohn-Sham equations for a situation, where the translational symmetry of the infinite crystal is locally broken by the perturbing impurity atom. The details of the method can be found elsewhere,⁹ and we restrict ourselves to note that potential perturbations on the Mo atoms and the eight nearest Na neighbors are determined self-consistently. Angular momenta up to l=4 are included and the form of von Barth and Hedin¹¹ for the exchange and correlation is used with parameters as chosen by Moruzzi, Janak, and Williams.¹² The correct embedding of the cluster of nine atoms into the infinite Na crystal is given by the Green's function of the host. Starting with a non-spin-polarized calculation a nonmagnetic solution is obtained which is then used as input for the spinpolarized calculation.

The nonmagnetic solution is found to be unstable and the self-consistency iterations clearly converge to a magnetic solution. The resulting local density of states for the spin-up and spin-down electrons on the Mo site is displayed in Fig. 4. The calculation yields a spin splitting (with reference to the centers of the spin-up and spin-down structures) of about 2.3 eV. The calculated moment is $M = 4.28 \mu_B$ giving a nonintegral spin S = 2.14, in quite satisfactory agreement with the experimental finding of strong 4d magnetism for Mo in Na. The calculated magnitude of the spin (and moment) is nicely consistent with the value $S = \frac{5}{2}$ resulting from our ionic-type analysis for the $4d^5$ configuration with L = 0. Interestingly, the calculation yields a large crystal-field splitting of about 1 eV between the Mo states of e_g and t_{2g} character as reflected by the double-peaked spin-up and spin-down structures in Fig. 4. Although the magnetism observed for the half-filled shell of Mo¹⁺ does not yield a direct proof against this prediction, the extrapolation of the experimental finding of crystal fields smaller or comparable to the LS coupling for Fe, Tc, and Ru ions in alkali metals^{1,4,5} to the present case suggest crystal fields being not larger than 0.2 eV for Mo in Na. Further theoretical and experimental studies are desirable to clarify the role of crystal fields for d ions in spmetals and in hosts with d band electrons (compare Ref. 5).

In summary, we have obtained new experimental and theoretical insight into the nature and strength of the basic interactions between isolated *d* ions and conduction electrons and ligands in very simple metallic hosts. Of special importance is the system Mo in Na, which reflects strong 4*d* magnetism of the half-filled 4*d* shell of Mo¹⁺ and permits a fair estimate of the local lattice structure. Quantitative spin-density calculations yield strong 4*d* magnetism for Mo in Na with an effective spin close to $\frac{5}{2}$ in good agreement with the experimental results. The local lattice structure of 3*d* and 4*d* ions in the



FIG. 4. Calculated local density of states (LDOS) on the Mo site for a Mo impurity in Na. Energies are given relative to the Fermi level of Na.

larger-volume K, Rb, and Cs hosts is governed by an internal contraction of the host lattice around the d ion. These contractions mainly arise from the fact that the bond strengths between the d cell and the host cells are much larger than the bond strengths between host ions along with the large compressibilities of the K, Rb, and Cs hosts. The proposed picture is supported by the experimental results known for 3d and 4d ions with localized d states in alkali-metal hosts, whereas these results are hard to explain within a picture of d ions on interstitial sites in an almost-rigid alkali-metal lattice.

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