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Molecular-orbital interaction in isolated transition-metal atoms

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Multiple-scattering calculations performed for the series of $M\mathrm{Ar}_{12}$ ($M=\mathrm{Mn}$, Fe, Co, Ni, and Cu) clusters have revealed that a strong admixture of the metal and Ar wave functions is found only for the Co cluster which could possibly explain the complexities in its absorption spectrum. A much slighter interaction is also found for the Fe cluster. However, in all the clusters studied the metal $4p$ level interacts significantly with the Ar $3p$ (valence) and $4s$ (conduction) crystal levels.

I. INTRODUCTION

The rare-gas matrix-isolation technique has been extensively used for studying highly reactive molecules and free radicals.[1] Particularly important has been the application of this technique to spectroscopic studies of isolated transition-metal atoms and small metallic clusters.[1,2] These studies are usually based on the assumption that the reactive species trapped in the chemically inert matrix are not significantly perturbed by the matrix itself. However, optical and ESR spectroscopies have revealed that the interaction between the isolated and host-lattice atoms is far from being negligible and that a variety of matrix-induced changes such as level shifts, additional splitting, and line broadening are commonly found. A great deal of work, both experimental and theoretical, has been devoted to the study of the trapped-atom–inert-matrix interaction. Complexities found in the spectra have been attributed to multiple-trapping sites,[3] a lowering of the symmetry of the trapping sites due to the presence of vacancies[4] or another metal atom as one of the nearest neighbors of the trapped atom,[5] long-range interactions between isolated atoms,[6] static distortion of the matrix (for example, a change in the crystal structure from fcc to hcp),[7] the dynamical Jahn-Teller effect in the excited state,[8] and "exciplex" formation between the excited metal atom and one of its rare-gas neighbors.[9]

Early theoretical studies on the matrix–isolated-atom interaction have been based on calculations using a Lennard-Jones-type potential.[3,8] This approach, which is essentially concerned with the binding potential between matrix and metal atoms is not very convenient for interpreting the absorption or ESR spectrum. More elaborate treatments considering spin-orbit and crystal-field interactions[7,10] and incorporating the dynamic Jahn-Teller effect[11] have been reported. Molecular-orbital (MO) cluster calculations have also been applied to the description of hyperfine interactions in the Mössbauer spectrum of Fe atoms[12,13] and Fe dimers[14] isolated in rare-gas lattices. A pseudopotential model has also been used to calculate the matrix perturbation on the optical spectra of isolated atoms.[15] A detailed survey of the different methods and approximations used to treat environmental effects on trapped atoms and molecules in rare-gas matrices can be found in Ref. 16.

In previous papers the multiple-scattering (MS) cluster model[17] has been applied to the description of the electronic structure and hyperfine interactions in both the Mössbauer and ESR spectra of transition-metal atoms isolated in an argon matrix.[18–20] In the present paper we shall analyze in detail the MO interaction between the isolated and the host-lattice atoms, i.e., the mixing between the metal and the lattice wave functions which combine to form MO's. Our calculations have shown that for the first-row transition-metal atoms in their ground state, this interaction is only present in the case of the Co atom isolated in a crystalline Ar matrix. For the unoccupied $4p$ metal level a significant metal-argon admixture is also found for all the isolated transition metals we have studied.

II. COMPUTATIONAL DETAILS

The spin-polarized MS cluster method in its muffin-tin form with Slater's $X\alpha$ local exchange has been applied to a cluster consisting of a transition-metal atom (Mn, Fe, Co, Ni, or Cu) and its twelve nearest-neighbor argon atoms. This cluster was designed to represent a transition-metal impurity occupying a substitutional site in the argon fcc crystal. This site has been shown both theoretically and experimentally to be the most likely for isolated transition-metal atoms.[15,21,22] The Ar-Ar distance was assumed to be that of bulk crystalline argon. Because of the lack of experimental information, the metal-Ar distance was assumed to be the same for all the clusters and equal to the Ar-Ar distance, i.e., we have not considered any distortion from the perfect cubic symmetry at the metal site.[21,22] All the calculations have been carried to self-consistency, all the electrons (core and valence) included in each self-consistent-field (SCF) cycle. Additional details of the computational procedures and the parameters used can be found in our previous papers.[18–20]

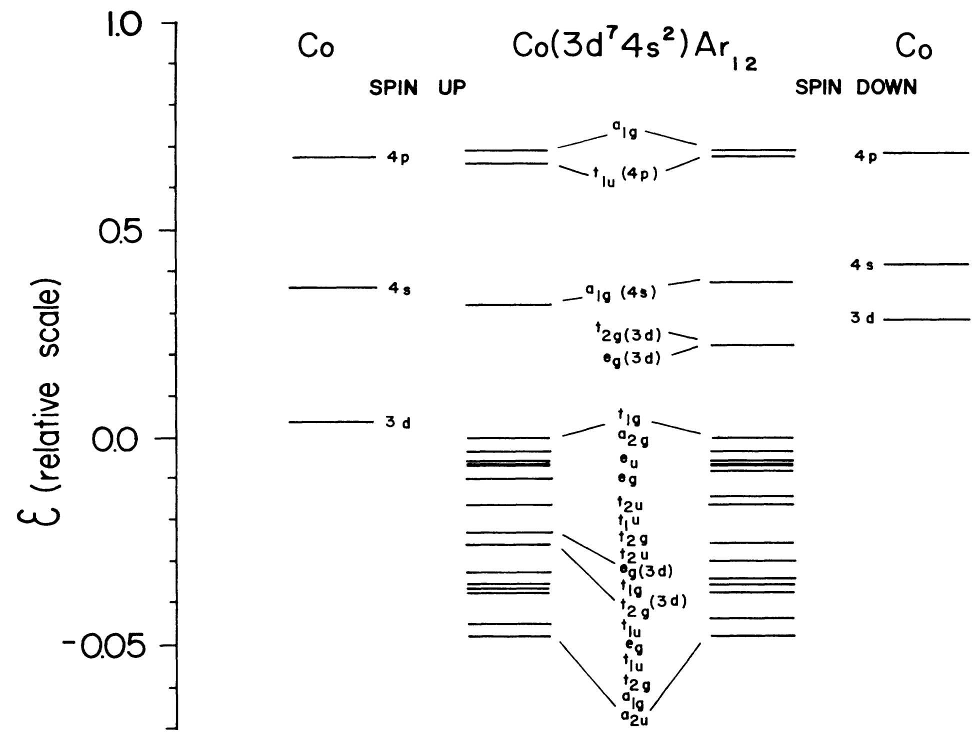

FIG. 1. Energy-level spectra for the CoAr_{12} cluster. The energies are referred to the highest occupied molecular-orbital level in the Ar $3p$ band (t_{1g}). The free-atom Co levels are also included.

III. RESULTS AND DISCUSSION

In Fig. 1 we present the calculated energy-level spectrum for the CoAr_{12} cluster obtained from our MS $X\alpha$ calculation. The optical and uv absorption spectrum of the Co atom in the Ar matrix is the most complex of all the spectra for the isolated first-row transition-metal atoms, exhibiting an extremely large level splitting.[2] Two explanations were suggested:[2] a large crystal-field splitting of some lines in the free-atom spectrum, or the possibility that the transitions seen in the isolated Co atom are due to very weak transitions in the gas phase. The first hypothesis is not very likely since such large splittings are not seen for other isolated atoms, and thus the second alternative was adopted as the most acceptable explanation. However, we think that the increased level splitting found in the optical spectrum of the Co in the Ar matrix originates from a completely different mechanism. In an earlier paper[23] the absorption spectrum of the Ag atom isolated in a Xe matrix was explained by considering a MO

TABLE I. Orbital energies and integrated charge density (in fractions of the electron charge) for orbitals of e_g and t_{2g} symmetry for the CoAr_{12} cluster (only Ar $3p$ and Co $3d$ levels are included).

Orbital	Orbital energy (−Ry)	Charge in muffin-tin spheres Co	Ar	Outer sphere	Interatomic
1 $e_g\uparrow$ (Ar $3p$)	0.783	0.191	0.782	0.001	0.026
1 $e_g\downarrow$ (Ar $3p$)	0.781	0.001	0.969	0.001	0.029
2 $e_g\uparrow$ (Co $3d$)	0.769	0.713	0.278	0.0	0.009
2 $e_g\downarrow$ (Ar $3p$)	0.755	0.001	0.983	0.004	0.012
3 $e_g\uparrow$ (Ar $3p$)	0.753	0.093	0.894	0.003	0.010
3 $e_g\downarrow$ (Co $3d$)	0.518	0.990	0.003	0.0	0.007
1 $t_{2g}\uparrow$ (Ar $3p$)	0.789	0.146	0.828	0.001	0.025
1 $t_{2g}\downarrow$ (Ar $3p$)	0.786	0.002	0.970	0.001	0.027
2 $t_{2g}\uparrow$ (Co $3d$)	0.772	0.590	0.398	0.001	0.011
2 $t_{2g}\downarrow$ (Ar $3p$)	0.761	0.002	0.979	0.003	0.016
3 $t_{2g}\uparrow$ (Ar $3p$)	0.756	0.261	0.727	0.002	0.010
3 $t_{2g}\downarrow$ (Co $3d$)	0.517	0.990	0.004	0.0	0.006

TABLE II. Integrated charge density (in fractions of the electron charge) in metal and argon spheres for the metal $3d$ e_g and t_{2g} orbitals for MAr$_{12}$ (M = Mn, Fe, Co, Ni, and Cu) clusters (argon values are given in parentheses). Values obtained for clusters with the free-atom ground-state configuration as the initial metal configuration.

Orbital	MnAr$_{12}$	FeAr$_{12}$	CoAr$_{12}$	NiAr$_{12}$	CuAr$_{12}$
$e_g \uparrow$	0.980 (0.013)	0.924 (0.072)	0.713 (0.278)	0.987 (0.009)	0.990 (0.002)
$e_g \downarrow$	0.974 (0.005)	0.985 (0.003)	0.990 (0.003)	0.991 (0.005)	0.992 (0.002)
$t_{2g} \uparrow$	0.974 (0.021)	0.912 (0.085)	0.590 (0.398)	0.978 (0.018)	0.990 (0.003)
$t_{2g} \downarrow$	0.975 (0.008)	0.985 (0.005)	0.990 (0.004)	0.989 (0.002)	0.992 (0.003)

interaction between the Ag $P_{3/2,\pm 3/2}$ level with the lowest unoccupied $6s$ level of the Xe atom. As a result of this interaction we cannot distinguish between metal and matrix orbitals as is usual in the crystal-field approach; instead we will have MO's formed by the combination of the metal and matrix wave functions. For the Co atom isolated in the Ar matrix the spin-up t_{2g} and e_g Co $3d$ levels are lying inside the Ar $3p$ band and in addition they are located in between the t_{2g} and e_g levels originating from the Ar $3p$ levels. This fact which has no equivalent for the other first-row transition-metal atoms isolated in the Ar matrix allows a strong admixture between the Co $3d$ and Ar $3p$ levels which distributes metal character among the Ar levels (see Table I). We should therefore expect a particularly complex absorption spectrum for the Co atom in the Ar matrix. It is also interesting to note that as a consequence of this mixing, which is considerably larger for the t_{2g} Co $3d$ level (59% of Co $3d$ character, 40% of Ar $3p$), the ordering of the levels resulting from the Co $3d$ splitting is reversed in relation to what would have been predicted on the basis of qualitative crystal-field theory and also with the results found for all the other transition metals in the Ar matrix. Finally it is worth mentioning that there is a fundamental difference between the Co in the Ar matrix and the Ag in the Xe matrix. In the first case the MO interaction is between ground-state levels, in the second the mixing is between levels in the excited state.

In the case of the FeAr$_{12}$ cluster, the spin-up e_g and t_{2g} levels also lie very close to the Ar $3p$ band (Fig. 1 in Ref. 18). A small admixture between the Fe $3d$ and the Ar $3p$ levels is also found: the spin-up e_g and t_{2g} Fe $3d$ levels have 92.4% and 91.2% of Fe $3d$ character and 7.2% and 8.5% of Ar $3p$, respectively. However, this mixing is much lower than in the CoAr$_{12}$ cluster and it probably has a small influence on the optical and Mössbauer spectra of the isolated Fe atoms.

The influence of the rare-gas lattice on the electronic structure of the isolated atoms has been described by considering two main contributions: the covalent (or crystalline) effect and the overlap distortion. Walch and Ellis[13] have analyzed the influence of each of these effects separately on the calculated Mössbauer Isomer Shift of the iron atom isolated in an argon matrix. Also, they studied the contribution of both these effects simultaneously through a non-self-consistent variational calculation on an FeAr$_{12}$ cluster. Near the Fe-Ar equilibrium separation it was found that the attractive potential dominates the overlap distortion. A detailed discussion of these results and those obtained with our MS cluster model for a similar FeAr$_{12}$ cluster can be found in Ref. 18. Forstmann and Ossicini[15] have described the interaction between the guest atom and the host lattice using a pseudopotential which includes the Coulomb (or crystalline) attraction and the overlap distortion. This calculation was used to interpret the shifts of the ground state and of the excited state for the Cu, Ag, and Au atoms isolated in rare-gas matrices. The attractive Coulomb potential dominates near the atomic nucleus while a strongly repulsive interaction was found over most of the atomic volume.[15] The results also indicate that the more contracted s function sees more attraction than does the p function and this is the reason for the "blue shifts" observed in the optical and uv absorption spectra. Our MS cluster calculations have always showed a marked atomic like character for the trapped atoms, i.e., covalent effects are almost negligible and the electronic structure of both the transition-metal atom and the host lattice are only slightly perturbed (see Table II). The only exception is the Co atom isolated in an argon matrix as has been discussed before. The overlap distortion is the most important interaction in the metal-Ar bonding and can explain the observed values for the hyperfine Mössbauer and ESR parameters in isolated neutral Fe (Refs. 18 and 19), Cu (Ref. 19), and Mn (Ref. 20) atoms. For rare-gas-isolated ions the present MS-cluster model seems to be inadequate since the polariza-

TABLE III. Integrated charge density (in units of the electron charge) for the $4p$ (t_{1u}) orbital for MAr$_{12}$ (M = Mn, Fe, Co, Ni, and Cu) clusters (the values given are for spin up and down, respectively).

	Metal $4p$	Ar ($3p$,$4s$)	Outer sphere	Intersphere
MnAr$_{12}$	0.429	0.213	0.056	0.302
	0.161	0.251	0.209	0.379
FeAr$_{12}$	0.425	0.212	0.061	0.302
	0.229	0.247	0.163	0.361
CoAr$_{12}$	0.415	0.213	0.069	0.303
	0.282	0.239	0.134	0.345
NiAr$_{12}$	0.394	0.217	0.081	0.308
($3d^84s^2$)	0.302	0.235	0.126	0.337
NiAr$_{12}$	0.250	0.239	0.161	0.350
($3d^94s^1$)	0.064	0.216	0.352	0.368
CuAr$_{12}$	0.362	0.222	0.100	0.316
($3d^94s^2$)	0.324	0.229	0.119	0.328
CuAr$_{12}$	0.227	0.238	0.180	0.355
($3d^{10}4s^1$)	0.064	0.215	0.355	0.366

tion of the rare-gas ligands by the ion charge will enhance the attractive van der Waals interaction (inductive effect).[20] At the SCF level, the metal–rare-gas interaction is always repulsive as has been shown in both Hartree-Fock[24] and MS calculations.

Finally, we have found that for all the first-row transition metals studied (Mn to Cu) there is a significant mixing between the metal $4p(t_{1u})$ unoccupied level and the Ar $3p$ and $4s$ levels transforming under the appropriate symmetry. This interaction is shown in Table III. We must not take the values given as a quantitative indication of the extent of the MO interaction in the excited state due to the diffuse nature of the metal $4p$ level (which largely lies outside the muffin-tin sphere, particularly in the case of the spin-down level) and the poor description of the Ar conduction band provided by the $X\alpha$ model. Therefore, transition-state calculations can not adequately reproduce the optical spectrum of the isolated atoms. We also can not evaluate accurately the influence of the overlap distortion on the excited levels. However, since these levels are largely extended over the ligand region it is very likely that they should be more affected by the repulsive overlap interaction than do the valence levels. This conclusion is in agreement with previous theoretical estimates.[15]

IV. CONCLUSION

It seems clear from our MS cluster calculations that the combination of both MO interactions, the ground-state interaction between the Co $3d$ and the Ar $3p$ band levels, and the interaction in the excited state between the Co $4p$ and the Ar $3p,4s$ band levels should largely be responsible for the complexities observed in the optical absorption spectrum of the Co atom isolated in a crystalline argon matrix. For the other isolated transition-metal atoms the MO interaction in the excited state should also be an important contribution to the complexities shown by their optical spectra. Recent experimental information seems to support the idea of a significant mixing between the metal $4p$ excited level and the Ar levels.[25]

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