sites and as such are expected to exhibit metallic conductivity.

Diffuse-reflectance spectra of $Na_3Cu_4S_4$ are consistent with this formulation. The spectra exhibit a reflectivity peak near 35 000 cm^{-1}, a very broad shoulder around 20 000 cm^{-1}, and a smeared out edge at 12–14 000 cm^{-1} which might be ascribed to the plasma edge. A reflectivity peak, ascribable to the 3d → 4s transition of Cu(I), often appears near 35 000 cm^{-1} in Cu(I) complexes. The observation of such a peak in $Na_3Cu_4S_4$ supports the photoelectron spectroscopy work by suggesting that $Na_3Cu_4S_4$ is a discrete Cu(I) complex.

A large number of alkali–copper–sulfide phases are now known, and it appears likely that all have interesting and unusual electrical properties. Furthermore, it appears that some of these materials are subject to chemical modification. We have, for example, prepared mixed Na/K analogues, but it is not yet clear whether these represent distinct phases or simply substitutional doping of KCu_4S_3 and $Na_3Cu_4S_4$. We will report on other alkali copper sulfides at a later date.

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Isolated Noble-Metal Atoms in a Neon Matrix

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By a pseudopotential method, the perturbation of the outer electronic s and p levels of Cu, Ag, and Au atoms by a Ne matrix is calculated. It is concluded that for Cu and Au the trapping site consists of three vacancies. Two sites of three and four vacancies give the two different "triplets" in the absorption spectrum of Ag.

Introduction

The optical spectra of Cu, Ag, and Au atoms isolated in a Ne matrix have been recently reported.[1-4] These systems have also been studied by ESR[5] and MCD.[3] The results of the experiments can be summarized as follows:

(a) Cu and Au atoms show three absorption lines, whereas for Ag five lines are observed, which are interpreted as two, partly overlapping triplets originating from Ag at two different trapping sites.[1]

(b) ESR experiments[5] show that Cu and Au atoms occupy multiple sites and that these atoms perhaps replace two or three atoms in each site.

The investigations using a neon matrix have to be compared with the analogous systems in argon, krypton, and xenon matrices.[6-19] The absorption spectra of Cu, Ag, and Au isolated in Ar, Kr, and Xe matrices consist typically of three absorption lines, generally blue shifted, compared to the two lines in the gas phase. In these cases it has been convincingly shown that careful annealing after deposition of the matrix leads to a single well-defined site of the impurity with very sharp absorption lines.[16] It was shown recently[18a] that for Ag in Kr UV irradiation can produce a secondary trapping site, which is also found in freshly deposited Ag/Kr systems, but annealing restores the unique well-defined matrix cage.[18a] For Ag in Ne, annealing leaves always two separate sites.[1] Also ESR[5] studies of these atoms in Ar, Kr, and Xe are in agreement with the optical results and indicate a single, uniform trapping site, most likely the substitutional site.

We have recently developed a pseudopotential method[20,21] for calculating the shifts of the outer s and p levels of isolated atoms in rare-gas matrices and so the transition energies. With this model the measured blue shifts of the absorption lines for Cu, Ag, and Au in Ar, Kr, and Xe matrices were derived for substitutional sites.[20] The situation of Ag in Ne is similar to the case of isolated alkali atoms in rare-gas matrices; for these atoms, for example Na in Ar, we clearly see two triplets, which are ascribed to Na in two different trapping sites.[22] By our pseudopotential method we have concluded that the different trapping sites for the alkali atoms are a metastable site of three vacancies and a stable trapping site of four vacancies.[21] In this work we analyze the matrix perturbation on the optical absorption spectra of Cu, Ag, and Au atoms in a Ne matrix.

The Pseudopotential and the Matrix Cage

We use the method developed in previous works.[20] We calculate with this model the energy levels of the metal atoms perturbed by rare-gas neighbors. Our Hamiltonian for the metal outer electrons is given by eq 1 with T as the kinetic

$$\mathcal{H}\Psi\rangle = (T + V_{\mathrm{A}} + \sum_{\mathrm{N}} V_{\mathrm{N}})\Psi\rangle = E\Psi\rangle \qquad (1)$$

energy, V_{A} the potential of the guest atom including the core

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Table I. Values of the Measured Line Shifts[a]

host	$\Delta(E_p - E_s)$, meV		
	Cu	Ag	Au
Ne	220	183, 241	254
Ar	292	315	308
Kr	177	198	178
Xe	36	44	−57

[a] The values are derived from the experimental data of Gruen and Bates[1] (Ag and Au in a Ne matrix), Grinter et al.[3] (Cu in a Ne matrix) and Kolb et al.[16] (Cu, Ag, and Au in Ar, Kr, and Xe matrices).

electrons in all filled shells, and V_N the potential of the matrix atoms, which is attractive. V_N is the Coulombic potential of a neutral rare-gas atom, supplemented by a $\rho^{1/3}$ Slater exchange term. The matrix wave functions $\varphi_N\rangle$ are imagined as weakly perturbed atomic orbitals in narrow bands with small amplitude on the guest atom, and the localized solutions $\Psi\rangle$ on the guest atom are approximated by atomic orbitals orthogonalized to the $\varphi_N\rangle$.

$$\Psi\rangle = (\varphi_A\rangle - \sum_N \varphi_N\rangle\langle\varphi_N\varphi_A\rangle)(1 - \sum_N|\langle\varphi_A\varphi_N\rangle|^2)^{-1/2} \quad (2)$$

When the sum over the crystal wave functions in the narrow rare-gas bands are approximated by a sum over atomic rare-gas functions $\varphi_{i,N}\rangle$ on each atom N, and if three-center integrals are neglected, one obtains the shifts of the atomic levels of the guest atoms due to the matrix:

$$E - E_A = \Delta E_A = \sum_N[\langle\varphi_A V_N \varphi_A\rangle - \sum_i\langle\varphi_A\varphi_{i,N}\rangle\langle\varphi_{i,N}V_N\varphi_A\rangle](1 - \sum_{i,N}|\langle\varphi_A\varphi_{i,N}\rangle|^2)^{-1} \quad (3)$$

We specialize (3) for different sites by different number and distances of nearest neighbors. We take into consideration the tetrahedral and octahedral interstitial sites, the substitutional site, as well as larger clusters of two, three, and four vacancies, which have been introduced into the discussion by Balling et al.[23] The two-atom vacancy cluster is essentially a substitutional site with a neighboring vacancy; the three vacancies are assumed to form an equilateral triangle with the impurity axially symmetric, and the four vacancy cluster is tetrahedrally arranged with the impurity atom at the center of symmetry.

With the geometry of the neighborhood fixed, we calculate the shifts for the ground state ΔE_s and for the excited state ΔE_p and so the shift of the absorption lines $\Delta(E_p - E_s)$, which can be compared with the experimental values. The experimental values for $\Delta(E_p - E_s)$ have been evaluated via crystal field analysis by the same method as used for noble-metal atoms in Ar, Kr, and Xe matrices.[16] The experimental data are taken from the measurements of Grinter et al.[3] for Cu and of Gruen and Bates[1] for Ag and Au. It is interesting to compare the measured shifts for the atoms isolated in a Ne matrix with the values for atoms isolated in Ar, Kr, and Xe matrices; these values are tabulated in Table I.

The measured line shifts decrease from Ar to Kr to Xe, while for Ne we find a smaller shift than for Ar, which means a break in the trend. The nearest-neighbor distances in the rare-gas crystals increase from Ne via Ar, Kr to Xe. The decrease of the shifts in Ne indicates that the noble-metal atoms in a Ne matrix need larger clusters of vacancies as trapping sites.

Results and Discussion

With the model for the matrix perturbation of the outer levels of the guest metal atom, we have calculated the level shifts of the outer s and p levels for Cu, Ag, and Au in a Ne matrix. By orthogonalization of the atomic wave functions of the metal atom to the wave functions of the rare-gas cage, we could obtain a nonlocal pseudopotential centered on each nearest-neighbor rare-gas atom, which perturbs the energy levels of the metal atom. A local approximation to this nonlocal pseudopotential shows its properties (see Figure 1 of ref 20). The potential consists of two terms: the first, which comes from the attractive screened Coulomb potential, dominates near the nucleus and in the outer region; the second, which is due to the orthogonalization terms, is repulsive and dominates over most of the atomic volume. The balance between these two contributions is very delicate and may be attractive or repulsive for the s or the p level of the guest atom depending sensitively on the metal atom–rare-gas atom distance.

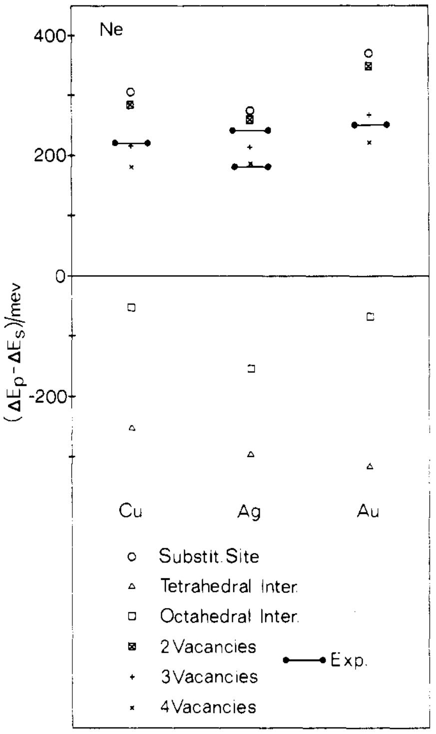

Figure 1. Calculated and measured values of the line shifts for Cu, Ag, and Au in a Ne matrix (•–•, measured values).

In Figure 1 the calculated values for the shift of the absorption lines $\Delta(E_p - E_s)$ are compared with the measured ones. The values are related to the tetrahedral and octahedral interstitial sites, to the substitutional site, and to the clusters of two, three, and four vacancies.

The two interstitial sites give strongly negative shifts, i.e., "red" shifts. For the substitutional site and for the three different clusters we calculate positive "blue" shifts, as found in the experiments. We discuss first the case of isolated Cu and Au atoms. For both metals the three-atom vacancy cluster gives shifts closest to the measured values. In the previous works with our model we have shown that the shift of the outer s level, the change in energy of the outer electron in the ground state, can be interpreted as the main contribution to the change in the total energy. Therefore we consider as repulsive the sites that give positive values of the s-level shift ΔE_s. Figure 2 shows the calculated s-level shifts (ΔE_s) for the different sites. We see that the small interstitial sites have a strongly repulsive character. Also the substitutional site and the two-vacancy cluster are weakly repulsive (only for the two-vacancy cluster the Au atom is very slightly bound, $\Delta E_s = -7$ meV). But the three-vacancy cluster already binds the s electron; the Cu atom is just on the margin of being bound ($\Delta E_s = +5$ meV). From the best agreement of the line shifts and the indications of the

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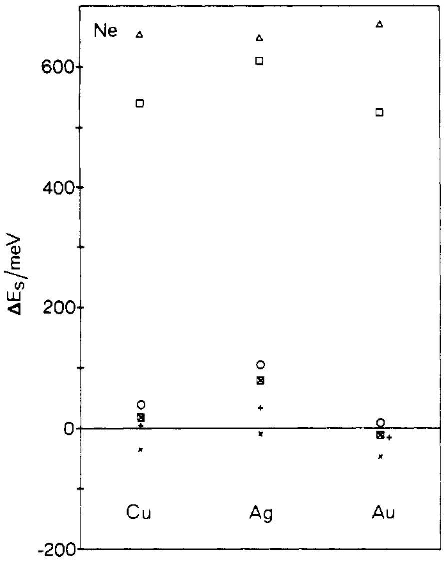

Figure 2. Calculated values of the s-level shifts for Cu, Ag, and Au in a Ne matrix.

binding site, we conclude that Cu and Au atoms sit in the Ne matrix in the large three-vacancy cluster; in this case the s-level can be even lowered by a few millielectronvolts by small displacements of the impurity atom from the point of high symmetry when the atom sits out of the plane of the equilateral triangle of the three vacancies. We now come to the isolated silver atom. In this case the experiments show two triplets of absorption lines; the associated average lineshifts are shown in Figure 1. Figure 2 shows that the substitutional site and the two-vacancy cluster are repulsive, that the three-vacancy cluster is weakly repulsive, and that only the larger four-vacancy cluster binds the s electron. From Figure 1 we see that for the narrow blue triplet the calculated values of the shift for the four vacancy cluster is very close to the experimental value and that the agreement between the calculated shift for the three-vacancy cluster and the experimental average line shift for the other blue triplet is good. Therefore, we conclude that the two trapping sites for Ag in a Ne matrix are the clusters of three and four vacancies, the second being the more stable.

This situation is similar to the case of the isolated alkali atoms. In this case too we have two distinct trapping sites, one more stable than the other upon annealing. In ref 21 we have shown that these two trapping sites are related to the three- and four-vacancy clusters and also here the later is more stable.

The difference between the isolated Ag atom and the Cu and Au atoms can be related to the more extended van der Waals diameter (D_{Cu} = 4.40 Å, D_{Ag} = 4.70 Å, D_{Au} = 4.60 Å)[24] or to the more extended s-wave function of the Ag atom.[25] By the more extended s function, the repulsive character of our pseudopotential is more strongly felt and larger distances are needed to accommodate the Ag atom. In the other rare-gas crystals for the noble-metal atoms the substitutional lattice site is large enough to bind the outer electron.

Conclusion

We have used a previously developed pseudopotential description of the influence of rare-gas matrices on the electronic levels of impurities in the case of Cu, Ag, and Au atoms isolated in a Ne matrix. We calculated the shift of the outer s electron and the shift of the absorption lines of the metal atom. We conclude that for Cu and Au the matrix-trapping site is a cluster of three vacancies. The two trapping sites for Ag are the more stable four-vacancy cluster with a smaller blue shift and the three-vacancy cluster, which gives a larger blue shift. The arguments were the close agreement between calculated and measured shifts of the absorption lines and binding of the outer s electron.

These results provide some insight into the different isolation behaviors of the Ne matrix compared to the other rare-gas matrices.

In Ar, Kr, and Xe matrices Cu, Ag, and Au atoms give only one triplet after careful annealing,[16,18,19] and ESR studies[5] give no evidence of multiple trapping sites. Recently we concluded that in these matrices the metal atoms are isolated substitutionally.[20] For the Ne matrix the absorption spectrum of Ag consists of two triplets[1] ESR[5] shows for Cu and Au evidence of multiple trapping sites, and also the measured blue line shifts for Ne show a break in the trend. We have shown that owing to the smaller nearest-neighbor distance in the Ne matrix the noble-metal atoms need larger vacancy cluster for the trapping sites. The very close agreement of our calculated shifts with the experiments leads us to conclude that our pseudopotential is a powerful tool to explain the different isolation behaviors of the rare-gas matrices and describes the interaction well enough to be used in further studies such as the deformation of the matrix cage from the cubic symmetry and the different trapping sites for atoms and ions.[26]

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Registry No. Cu, 7440-50-8; Ag, 7440-22-4; Au, 7440-57-5.

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