

Electronic properties of alkali-metal–gold compounds

C. Koenig,* N. E. Christensen,[†] and J. Kollar[‡]*Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany*

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Self-consistent relativistic band-structure calculations have been performed for the alkali-metal–gold compounds, MAu ($M=Li, Na, K, Rb,$ and Cs) in the CsCl structure. CsAu and RbAu are semiconductors at normal pressure, whereas the other compounds—in the assumed CsCl structure—are metallic. Total-energy calculations are used to derive equilibrium volumes, bulk moduli, and heats of formation. The calculations suggest that RbAu undergoes an insulator-metal transition at a moderate pressure, ≈ 30 kbar. KAu is the metallic compound in the series which is “closest” to being an insulator; a uniform expansion corresponding to a pressure of ≈ -30 kbar would cause a metal-insulator transition.

I. INTRODUCTION

Metallic alloys obey, in most cases, “Vegard’s rule,” which states that the volume per alloy formula unit equals the sum of the pure-metal atomic volumes. Covalent compounds, such as GaAs, have, in general, volumes that are larger than this ideal volume, whereas compounds with ionic bonding are known to have smaller volumes. All intermetallic compounds in the alkali-metal–gold series MAu ($M=Li, Na, K, Rb,$ and Cs) exhibit strong deviations from Vegard’s rule. They are contracted by 30–40%, LiAu being the least compressed and CsAu being the compound with the largest deviation. The volume contraction of stoichiometric 50 at. %–50 at. % CsAu has been known for a long time¹ and has been associated with a strong ionic character.

The particularly large volume contraction upon alloy formation in the alkali-metal–gold series is one reason why their electronic structures are of theoretical interest. Another reason is that not all alloys are metallic. Proceeding through the series from LiAu to CsAu, a metal-insulator transition seems to occur between KAu and RbAu. This has been confirmed experimentally for the liquid phase,^{2,3} and the optical data by Spicer *et al.*¹ showed that solid CsAu is a semiconductor with a gap of ~ 2.6 eV. The electronic structure of CsAu has recently been studied experimentally by x-ray photoelectron spectroscopy (XPS) and photoemission spectroscopy.^{4–6} In addition, theoretical investigations of the band structures agree with this observation.^{6–9} The formation of the insulating gap in CsAu is associated with formation of bonds of strong ionic^{7,9} character, gold being the negative ion. The calculations in Refs. 7 and 9 also showed that a gap only forms in the theoretical model when relativistic effects are included, the mass-velocity shift of the Au 6s states being particularly important. It was further shown⁹ that the Cs 5s and 5p corelike states are important in the alloy-formation process.

In this work we wish to study trends in the series of alkali-metal–gold alloys, and we do this by presenting results of self-consistent (linear muffin-tin orbitals¹⁰ (LMTO) band-structure calculations. The calculated total energies and their variations with volume are used to

derive equilibrium volumes, bulk moduli, and heats of formation. Since relativistic effects are essential in a theoretical band model for these compounds, they are included in all cases.

The paper is structured as follows. Section II contains a brief description of the methods of calculation, and also contains a compilation of the crystal-structure data used in this work. The results of total-energy calculations (bulk moduli, heats of formation, and equilibrium volumes) are given in Sec. III. The relativistic band structures for the alkali-metal–gold compounds in the CsCl structure are shown in Sec. IV, and in Sec. V we discuss the gaps in the semiconducting alloys.

II. MODEL PARAMETERS: CRYSTAL-STRUCTURE DATA

Few experimental data are available for the solid alkali-metal–gold compounds. This is partly due to difficulties in the sample preparation. Further, the analysis of crystal-structure data is not straightforward. The structures of the metallic compounds (LiAu, NaAu, and KAu) are intricate and not well known. LiAu is reported¹¹ to have a CsCl structure, but the existence of this phase has been confirmed¹² only for Li-Au compounds with 44–45 at. % Au and not for stoichiometric LiAu. The existence of NaAu and KAu has been established,¹² but their crystal structure is completely unknown. The case of the two most ionic compounds, RbAu and CsAu, is simpler; they both crystallize in the CsCl structure and their lattice parameters have been measured.¹² In previous theoretical studies^{7,11} of trends in the electronic properties of the alkali-metal–gold compounds, the crystal structure has been assumed to be CsCl in all cases. Pending new experimental data we have had to make the same assumption in the present work.

The fact that we have to assume hypothetical crystal structures for the metallic compounds complicates, of course, the comparison of calculated quantities to (the sparse) experimental results. This becomes even more difficult since we, in addition, must devise a method for estimating “experimental” lattice dimensions. Huang and Liu,¹¹ followed by Hasegawa and Watabe,⁷ used interpo-

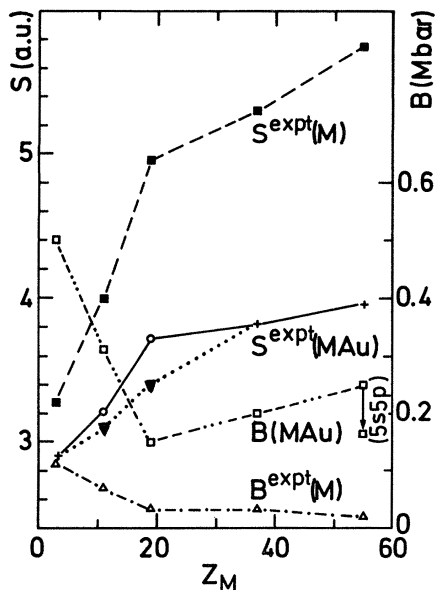


FIG. 1. Plot vs alkali-metal atomic number (Z_M) of the following. $S^{\text{expt}}(M)$: Experimental Wigner-Seitz radius of the pure alkali metals. $S^{\text{expt}}(MAu)$: +, known experimental atomic radii in the compounds. ($4\pi/3S^3$ denotes the cell volume); ▼, derived by linear interpolation of S (Ref. 11); ○, present estimate from interpolation of C [see Sec. II, Eq. (1)]. $B^{\text{expt}}(M)$: Experimental bulk moduli of the pure alkali metals. $B(MAu)$: Calculated bulk moduli of the compounds at the "experimental" volume. The arrow indicates the effect of treating the Cs $5s$ and $5p$ states as band states.

lated values of the lattice parameter a for NaAu and KAu, assuming a linear relation between a and Z_M , the atomic number of the alkali constituent. The "experimental" lattice constants obtained in this way for NaAu and KAu were 3.33 and 3.65 Å (from Ref. 11), and 3.44 and 3.71 Å (from Ref. 7), respectively. In view of the large uncertainties already inherent in the model, this interpolation is probably sufficiently accurate. Nevertheless, we have chosen another procedure. As follows from Fig. 1, the curve showing the experimental¹² Wigner-Seitz radius $S(M)$ of the pure bcc metals versus Z_M has a marked change of slope at K . This is probably related to the presence of filled d states in the cores of Rb and Cs. Since

these core states are only slightly affected by alloying, the same slope variation must be expected in an $S(MAu)$ -vs- Z_M curve for the compounds. We define $S(MAu)$ as the radius of a sphere having the average atomic volume in the compound, and a ratio C is defined through

$$C = \frac{S^3(M) + S^3(\text{Au})}{2S^3(MAu)} \quad (1)$$

This quantity is a measure of the deviation from Vegard's rule. C depends very sensitively on the values of the atomic radii since they enter cubed. The three experimental room-temperature values¹² of C for LiAu, RbAu, and CsAu are, to a very good approximation, on a straight line (Fig. 2). The C values for NaAu and KAu deduced from the lattice parameters given in Ref. 11 are very far from this line, and would suggest peculiarities of these compounds. We consider it more reasonable to assume a linear variation of C through the series, and we deduce "experimental" S values for NaAu and KAu by linear interpolation in C vs Z_M . In doing this we reproduce, for the alloy, the slope variation observed in the $S^{\text{expt}}(M)$ - Z_M curve for the pure metals. This is shown in Fig. 1 [the curve $S(MAu)$]. As follows from Sec. III, this procedure is supported by the theoretical calculation of the equilibrium volumes.

Table I gives the experimental lattice dimensions chosen in the way described above. In addition, Table I contains electron-configuration information relevant for the band calculations. The LMTO band-structure calculations presented here used a "frozen-core approximation," i.e., the inner-electron wave functions were taken from the self-consistent *atomic* calculations, but renormalized to the atomic spheres in the compound. Only the "band states," those not included in the cores listed in Table I, were adjusted during the self-consistency cycles. The frozen-core configuration of the Au is $[\text{Xe}]4f^{14}$. In the present calculations we also treat the Rb($4s, 4p$) and Cs($5s, 5p$) states as frozen-core states (see Table I). As shown earlier,⁹ this leads to systematic errors which are particularly large in the high- Z_M end of the series (CsAu). Errors due to the frozen-core approximation are expected to be small for LiAu and NaAu. This follows from calculations of atomic core charge densities at distances beyond the atomic-sphere radii.

The self-consistent crystal potentials were generated by

TABLE I. Electronic configuration in the core (kept frozen during self-consistency iterations), lattice dimensions, and results of total-energy calculations for the alkali-metal-gold compounds. S^{th} and S^{expt} are the calculated and experimental equilibrium values of the atomic radius (an asterisk denotes a value estimated as explained in Sec. II). The calculated bulk modulus is given at the experimental (B_{te}) as well as at the theoretical (B_t) equilibrium volume. The heat of formation ΔH is given in the last column. The numbers given for CsAu in parentheses are obtained (Ref. 9) from calculations where the Cs $5s$ and $5p$ states are treated as (self-consistent) band states.

M	Core	S^{th} (a.u.)	B_t (Mbar)	S^{expt} (a.u.)	B_{te} (Mbar)	ΔH (mRy)
Li	$1s^2$	2.81	0.80	2.883	0.50	-27
Na	$[\text{He}] 2s^2 2p^6$	3.12	0.52	3.21*	0.31	-8
K	$[\text{Ne}] 3s^2 3p^6$	3.60	0.28	3.72*	0.15	-0.8
Rb	$[\text{Ar}] 3d^{10} 4s^2 4p^6$	3.79	0.23	3.820	0.20	+5
Cs	$[\text{Kr}] 4d^{10} (5s^2 5p^6)$	4.08(3.86)	0.16	3.968	0.25(0.16)	+26(-2)

LMTO band-structure calculations including the relativistic corrections apart from the spin-orbit (SO) coupling, i.e., in a so-called scalar-relativistic scheme. Spin-orbit coupling was finally taken into account as a perturbation to the scalar-relativistic self-consistent Hamiltonian. Exchange and correlation were treated in the local-density approximation.¹³ In all cases, f partial waves were included, and the band structures were calculated with the inclusion of the so-called “combined correction terms.”¹⁰ The last iterations in each self-consistency cycle were performed on a grid corresponding to 969 \vec{k} points in the irreducible wedge of the simple-cubic Brillouin zone.

In the calculation of heats of formation (Sec. III) small differences between total energies have to be found. The \vec{k} -space integrations are performed by means of the tetrahedron method,¹⁴ and all band calculations for the alloy and the pure metals use identical divisions in \vec{k} space; they are all also done in the CsCl structure, even for gold. In this way we reduce small errors due to a somewhat unexpedient¹⁵ way of dividing \vec{k} space, and further, we avoid uncertainties due to the different accuracy of the LMTO for fcc and bcc structures.

The atomic-sphere radii used in the LMTO calculations for the alloys were chosen to be equal for Au and the alkali-metal constituent. This choice of sphere radii affects, of course, the calculated values of charge transferred from the gold sphere to the alkali-metal sphere. The definition of such charge changes as “charge transfer” has, in general, no physical meaning except for the cases where electrons are transferred to the very *inner* part of a sphere [this is the case only for the most ionic compound CsAu (Refs. 7 and 9)]. The common Au- and M -sphere radius is, in the following, denoted by S [$(4\pi/3)S^3$ is half of the volume of the simple-cubic cell].

III. TOTAL ENERGIES AND RELATED QUANTITIES

For each of the MAu compounds self-consistent calculations were performed for a series of S values around the “experimental” (see Sec. II) equilibrium values. From calculations of the total electronic pressures—of course, including Madelung contributions—the theoretical equilibrium values S^{th} were derived as well as the bulk moduli.

A. Equilibrium

The values for S^{th} , at which the theoretical pressure is zero, are listed in Table I. They are, for the compounds which are known to exist in the CsCl structure (LiAu, RbAu, and CsAu), very close to the experimental radii S^{expt} (Table I). From the theoretical S values we have calculated the theoretical C ratios [Eq. (1)], also using theoretical pure-metal volumes.^{16,17} The results are shown in Fig. 2 as solid circles connected with a dotted line. As mentioned earlier, the outer-core states are important for the crystal binding, and this is particularly true for CsAu.⁹ The effect of treating the Cs $5s$ and $5p$ states as band states, and including their adjustment during the self-consistency cycles, is indicated with an arrow in Fig. 2. The value of S^{th} for CsAu with frozen $5s$ and $5p$ states is 4.08 a.u., whereas relaxation to self-

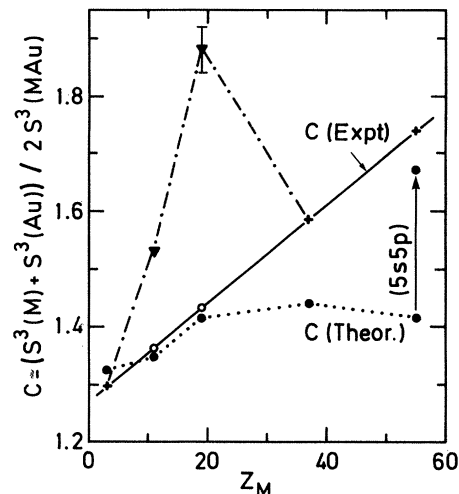


FIG. 2. Volume ratio C [see Eq. (1)] describing the deviation from Vegard's rule. +, experimental results; \circ , present estimate of C for NaAu and KAu; \bullet , theory. The dotted line connects theoretical results where the outer s,p core states were kept frozen. The arrow indicates the effect in the theoretical value of treating Cs $5s$ and $5p$ states as band states self-consistently. The solid-inverted triangles (\blacktriangledown) connected by a dashed-dotted line correspond to the S values derived in Ref. 11.

consistency of these states reduces S^{th} to 3.86 a.u. A similar, but quantitatively smaller, effect is expected for RbAu, if the $4s$ and $4p$ states are treated as band states—and to an even lesser extent, for KAu. With these corrections the *theoretical* relation between C and Z_M will approximately correspond to a straight line in Fig. 2, not far below the experimental one. This supports our choice (Sec. II) of the procedure for estimating “experimental” lattice spacings for NaAu and KAu in the hypothetical CsCl structure.

B. Compressibility

The bulk modulus

$$B = -V \frac{\partial P}{\partial V} \quad (2)$$

was derived from the calculated pressure-volume (P - V) relations. The values obtained for B at the theoretical as well as at the experimental atomic radii are given in Table I. The variation of B with Z_M is similar to that of the pure-metal moduli¹⁸ (see Fig. 1), but with all values being larger for the compounds due to the alloying with gold. Furthermore, here, the effect of treating the Cs($5s,5p$) states as band states is indicated with an arrow (Fig. 2). This correction increases the similarity between the pure-metal and the compound values through the series even more.

C. Heat of formation

The heat of formation per atom at zero temperature¹⁹ and pressure is defined as

$$\Delta H = \frac{1}{2}(E_{MAu} - E_{Au} - E_M), \quad (3)$$

TABLE II. Fermi levels, partial occupation numbers (n_i) per spin, and excess number (ΔQ) of electrons in the M atomic sphere in MAu compounds without spin orbit splitting. (Concerning the physical significance of ΔQ , see text.) Number in parentheses denotes Cs $5s$ and $5p$ states treated as band states.

M	E_F (Ry)	Au				M				ΔQ
		n_s	n_p	n_d	n_f	n_s	n_p	n_d	n_f	
Li	-0.1646	0.451	0.206	4.536	0.014	0.216	0.390	0.133	0.052	0.584
Na	-0.2394	0.575	0.147	4.705	0.009	0.179	0.225	0.117	0.041	0.123
K	-0.2683	0.742	0.061	4.842	0.006	0.088	0.116	0.112	0.031	-0.303
Rb	in gap	0.770	0.048	4.861	0.006	0.075	0.092	0.114	0.031	-0.372
Cs	in gap	0.800	0.033	4.882	0.007	0.055	0.069	0.118	0.033	-0.445(-0.71)

where E_{MAu} is the total energy calculated for the compound and E_{Au} and E_M are the energies of the constituent pure metals. All three energies are calculated at the experimental volumes, and as mentioned in Sec. II, they are all calculated for CsCl structures. The results are displayed in Table I. They show that going through the series from LiAu to CsAu, the compound becomes less and less stable. We only want to study the trends, and do not emphasize too much the actual values obtained for ΔH . All values should in fact be negative—RbAu and CsAu do exist. As found previously,⁹ the outer-core states are important for the binding of the crystals in the high- Z_M end. In Table I the value⁹ for ΔH of CsAu with inclusion of Cs $5s$ and $5p$ states as band states is added in parentheses. A similar correction should be applied to KAu and RbAu if more quantitatively correct results for ΔH are needed.

IV. BAND STRUCTURES

A. Scalar-relativistic band structures

The self-consistent scalar-relativistic band calculations show that the compositional metal-insulator transition in the alkali-metal-gold series occurs between KAu and RbAu. KAu is a metal with a low density of states at the Fermi level built up from small pockets of electron states around X and holes around R . CsAu and RbAu are, in this model (local-density approximation), insulators with indirect gaps of 1.22 and 0.33 eV, respectively, between the top of the gold $6s$ band at R_2 , and the X_1 level (see Fig. 1 in Ref. 9). The X_1 state is predominantly of Au p and Cs s character. The partial numbers of occupied states on each site for the alloys are given in Table II. Going from LiAu to CsAu, this table shows that the s and p states are progressively being emptied on the M sites, whereas the number of occupied s and d states increase on gold. These latter states constitute, for RbAu and CsAu, the valence bands. Contrary to the results of the non-self-consistent Korringa-Kohn-Rostoker (KKR) calculations by Overhof *et al.*,⁶ we find that the gold d states are located inside the energy regime of the Au $6s$ states, with which they are strongly hybridized.

Table II also gives ΔQ , the excess number of electrons in the M sphere. The values decrease gradually through the series with increasing Z_M . Note, that only for the most ionic cases, CsAu, and to some extent RbAu, can

this number be considered as a "charge transfer" (Sec. II and Ref. 9). The value of ΔQ (-0.71) given for CsAu in parentheses was obtained with the Cs $5s$ and $5p$ states treated as self-consistent band states. The numerically large contribution to ΔQ from these corelike states (≈ -0.27) again reflects their importance in the alloy-formation process.

The total change of radial electron density upon alloy formation in CsAu was illustrated in Ref. 9. Here we show (Fig. 3) that the main contribution to the charge transfer is due to removal of s and d electrons from the outer part of the Cs sphere [Fig. 3(a)] to s states in the inner part of the gold sphere [Fig. 3(b)]. Note the difference between the trends through the series of n_i listed in Table II and the results given in Fig. 3. The former shows how the hybridization, for example, between Au s

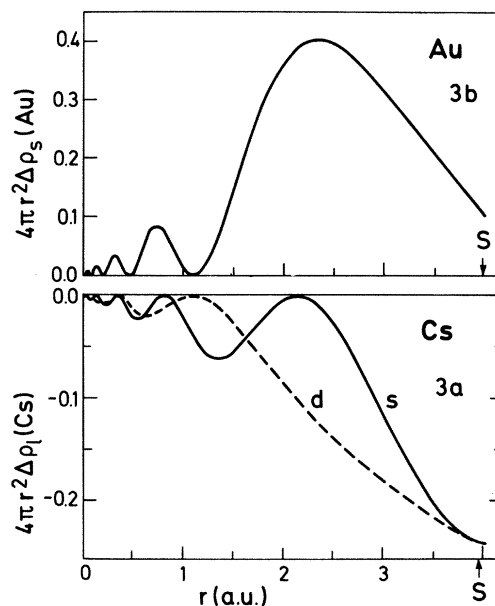


FIG. 3. CsAu. Change in radial partial charge density for s and d states in the Cs sphere and s states in the Au sphere, associated with the alloy-formation process. The self-consistent charge densities of the pure metals which were subtracted from the alloy density were calculated for bcc Cs and Au compressed (expanded) to the atomic volume of the constituents in the alloy. (Other partial charge changes are not shown since they are small. For total change, see Ref. 9.)

and Cs p states, varies through the series. Figure 3 shows, for a given compound, how the alloy process itself is related to charge redistribution. The pure-metal calculations used in the calculation of the charge differences shown in Fig. 3 were performed with an atomic volume equal to that of the constituent in the *alloy*.

B. Spin-orbit coupling

The spin-orbit operator

$$\xi(\vec{s} \cdot \vec{l}) = \frac{1}{c^2} \frac{2}{r} \frac{dV(r)}{dr} \frac{1}{2} \begin{pmatrix} l_z & l_- \\ l_+ & l_z \end{pmatrix} \quad (4)$$

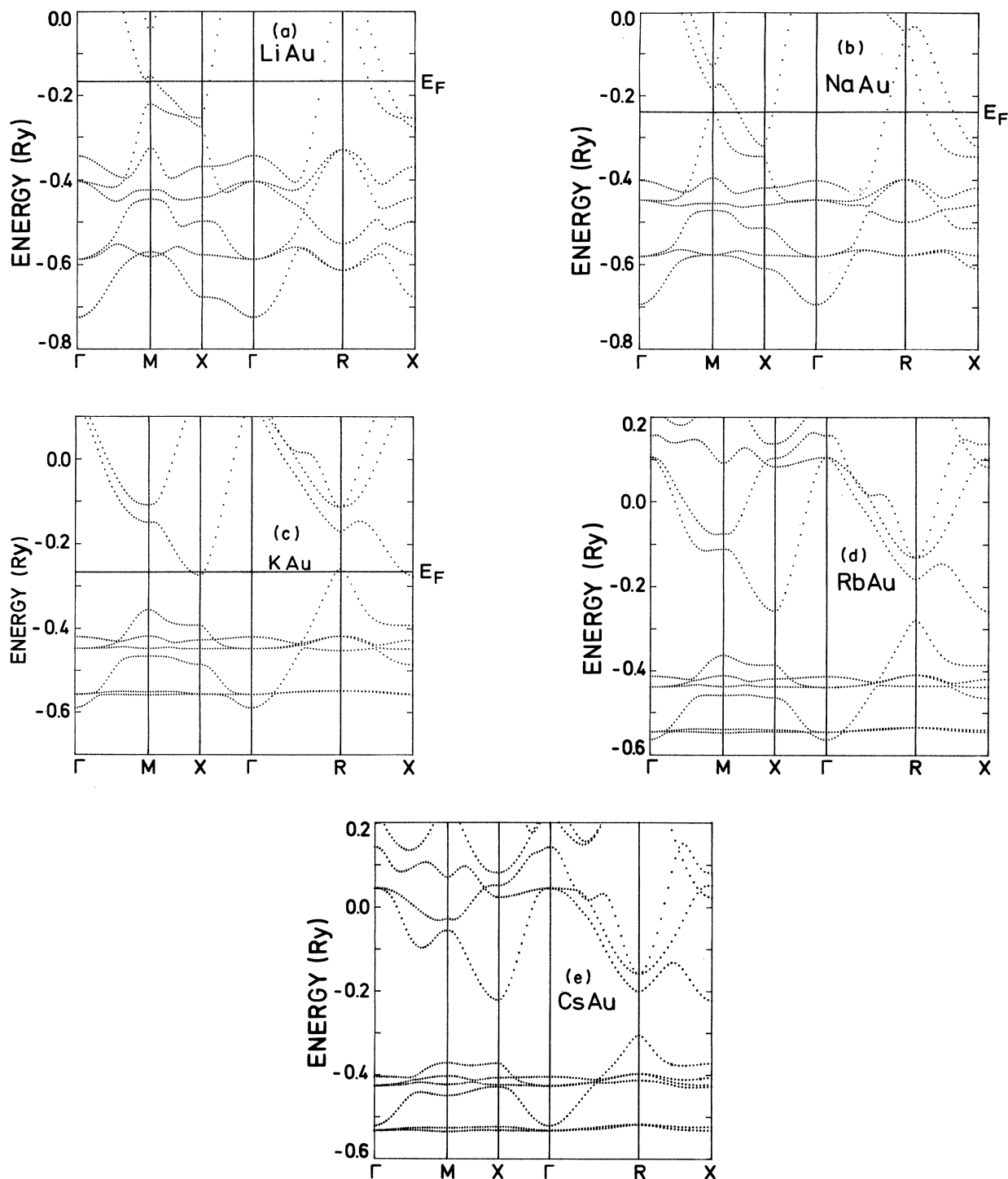


FIG. 4. (a) Band structure of LiAu, $S=2.883$ a.u.; (b) of NaAu, $S=3.21$ a.u.; (c) of KAu, $S=3.72$ a.u.; (d) of RbAu, $S=3.820$ a.u.; (e) of CsAu, $S=3.968$ a.u.

was added as a perturbation to the Hamiltonian containing the self-consistent scalar-relativistic potential $V(r)$.

The SO parameter ξ_{l0} at the center¹⁰ C_l of an l band is (in a.u.)

$$\xi_{l0} = 2 \int_0^S \frac{1}{rc^2} \frac{dV(r)}{dr} \phi_l^2(C_l, r) r^2 dr. \quad (5)$$

For pure gold, ξ_{20} , the SO parameter at the $5d$ -band center is²⁰ 47.9 mRy. In the alkali-metal-gold compounds, ξ_l calculated at the center of gravity of the occupied Au d density of states (in RbAu, 4 mRy above C_2) is very close to this value: 46 mRy in RbAu and 48 mRy in LiAu. The SO parameter for the $6p$ states of gold is of

the same order of magnitude, whereas all other SO parameters are negligibly small. The main effect of the SO coupling in the MAu compounds then is the splitting of the Au $5d$ band into two widely separated (by ≈ 1.5 eV) narrow bands corresponding to the $5d_{3/2}$ and $5d_{5/2}$ components. This can be seen in the dispersion curves [Figs. 4(a)–4(e)] and the density-of-states functions [Figs. 5(a)–5(e)]. Further, the $R_{25'}$ level is split into two levels, R_8^+ and R_7^+ . In RbAu and CsAu, this splitting is not sufficiently large to change the gap to a direct one. Even when SO coupling is included, $E(X_1) - E(R_2')$ (single group notation) is the smallest. The indirect gap is even slightly reduced (by ≈ 2 mRy) when SO splitting is included, although neither of the states are split.

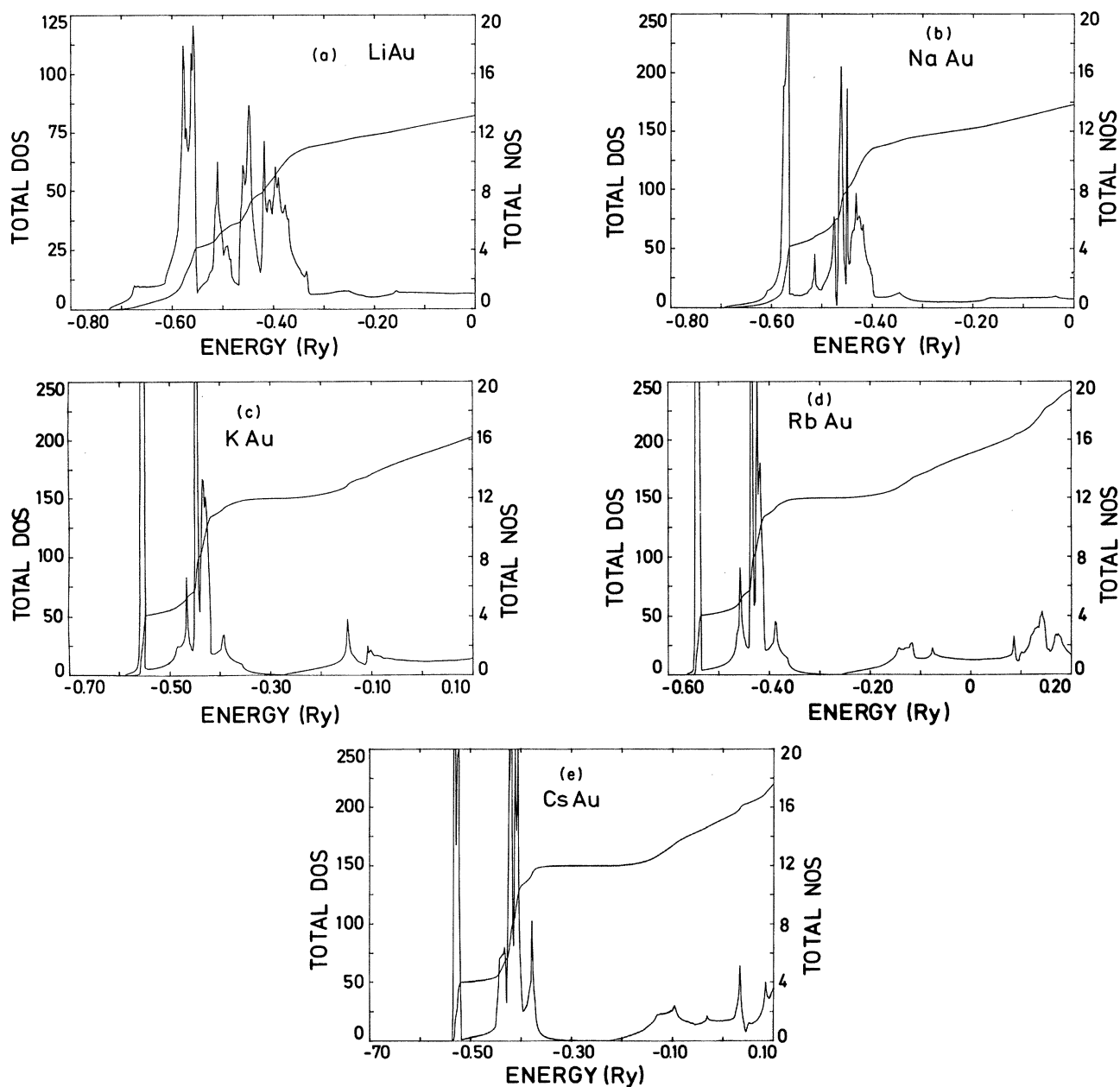


FIG. 5. (a) Density-of-states and number-of-states functions for LiAu; (b) NaAu; (c) KAu; (d) RbAu; (e) CsAu.

V. GAPS IN CsAu AND RbAu

In agreement with experiments, our calculations show that CsAu and RbAu are semiconductors in the CsCl structure. The importance of relativistic effect on the gap formation was discussed previously.⁹ For illustration, we include here (Fig. 6) a nonrelativistic band structure of CsAu. It shows that the gap is closed due to the omission of the large mass-velocity shift of the top of the Au 6s band. If the nonrelativistic density-of-states function is considered, it will be found to be very similar to the one calculated in the (scalar-) relativistic scheme in the energy range around E_F . At E_F the nonrelativistic density is very low since the gap is closed only in a very small region in \vec{k} space.

In all compounds there is a strong hybridization between Au 6s states and M s states. In a simple two-band model this causes the formation of a hybridization gap which separates bonding states from antibonding states. In CsAu and RbAu the relativistic shifts place the s states relative to the other bands in such a way that this hybridization gap becomes a genuine gap in the full band structure. It has been observed experimentally for (liquid) CsAu that small deviations from stoichiometric composition dramatically change the electrical conductivity. Essentially, only the 50 at. %–50 at. % alloy seems to be semiconducting. Similar effects may be expected for the solid phases of CsAu and RbAu. We do not associate such effects with dramatic changes in the band structure when the composition is slightly altered. Instead, a change in occupation is expected—addition of Au at the expense of Cs creates holes in the filled Au 6s band, whereas electrons fill up the bottom of the Cs s band when Cs is added. Asymmetry in the conductivity-versus-composition relation around stoichiometry would then reflect differences in mobility of the two types of carriers.

KAu is on the metallic side and RbAu on the insulating side of the compositional metal-insulator (M-I) transition. Only small changes in the volumes are needed for

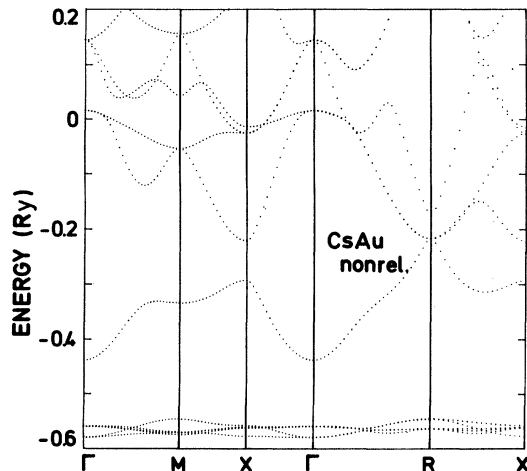


FIG. 6. Nonrelativistic, self-consistent band calculation for CsAu showing that the gap does not exist in this model.

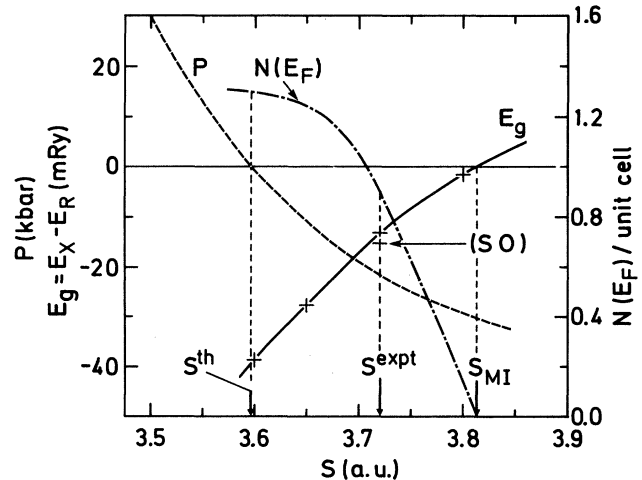


FIG. 7. KAu. Variation with atomic radius S of P , pressure (dashed line), $N(E_F)$, density of states at the Fermi level (dashed-dotted line), and E_g , $E(X_1) - E(R'_2)$, which, when positive, specifies the gap in the semiconducting phase. SO shows the effect of spin-orbit coupling.

these alloys to induce transitions from metallic to insulating phases. Figure 7 shows, for KAu, the variation of the energy difference $E_g \equiv E(X_1) - E(R'_2)$, the density of states at E_F , and the pressure with atomic radius. It follows that a gap—the indirect $R-X$ gap—is formed when S is larger than $S_{M-I} \approx 3.82$ a.u. (A slightly larger expansion is necessary due to SO corrections.) The uniform expansion necessary to produce the metal-insulator transition in KAu corresponds to a pressure of ≈ -30 kbar. The metallization of RbAu under pressure is illustrated in Fig. 8. Although the SO splitting of $R_{25'}$ increases somewhat under pressure, the gap remains indirect ($R-X$) for all reduced volumes until metallization is reached. As follows from Fig. 8, the calculations predict the metal-insulator transition to occur at approximately 30 kbar (28 kbar with SO and 32 kbar in the scalar-relativistic case).

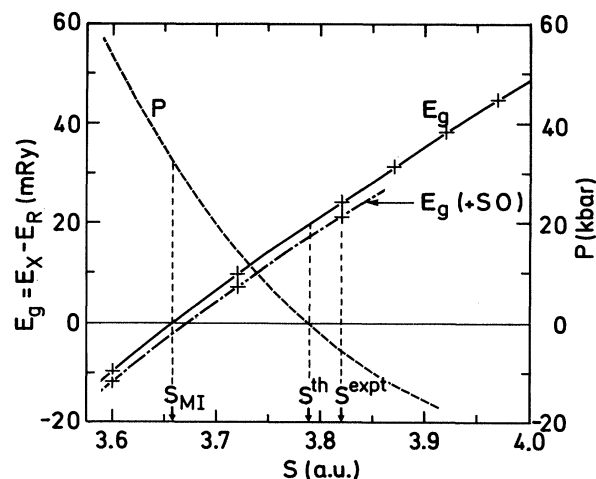


FIG. 8. RbAu. Pressure (P) and gap (E_g) as a function of atomic-sphere radius. Metallization occurs when $E_g = 0$; i.e., at $P_{M-I}^S = 32$ kbar in the scalar-relativistic model. SO coupling reduces the transition pressure to 28 kbar.

The difference between S^{th} and S^{expt} (Fig. 8) gives an indication of the uncertainties (partly due to temperature effects) in our pressure calculations. A simple parallel displacement of the P - S curve so that $P=0$ at S^{expt} would increase P_{M-I}^S to ~ 38 kbar.

It is well known that the local-density approximation always leads to too small gaps in band models of insulators. This is also the case here. For CsAu the experimental gap is¹ ~ 2.6 eV, whereas our calculated value is 1.22 eV, i.e., less than half of the experimental result. This does not imply, however, that the calculated metallization pressures are correspondingly in error. The existence of a Fermi surface in a metal and its shape and dimensions are true ground-state properties which are well described by the local-density scheme. This means that this scheme must be well suited for predictions of crystal volumes at which the Fermi surface appears, i.e., for the prediction of the metallization volumes. Once a gap is formed, the calculated value may differ substantially from the experimental one, but its very existence should be correctly predicted.

VI. CONCLUSIONS AND SUMMARY

The electronic properties of stoichiometric alkali-metal-gold compounds have been studied by means of self-consistent LMTO band calculations. In all calculations it was assumed that the CsCl structure is present, although NaAu and KAu crystallize in more complicated structures. Since these are not known, we assumed the presence of the CsCl structure with lattice parameters deduced from the trend through the series of the deviation from Vegard's law. In the present theoretical model, CsAu and RbAu are found to be semiconductors, whereas the other compounds are metals. The heat-of-formation calculations show that the stability of the compounds vary

gradually through the series, LiAu being most stable and CsAu the least stable compound. This reflects, maybe, the observation that CsAu is not stable¹ in the atmosphere, it must be prepared under vacuum. The calculated equilibrium volumes are very close to the experimental results, where available, and they therefore agree with the observation that the alkali-metal-gold compounds show strong deviations from Vegard's law. This deviation increases through the series; it is smallest for LiAu and largest for CsAu. RbAu and CsAu—the semiconductors—are the most ionic compounds and simultaneously those for which the deviation from Vegard's law is most marked. The ionic character of the bonding in CsAu has been illustrated by calculation of partial charge differences. Electrons of s and d character are removed from the outer regions of the "Cs spheres" into the inner part of the "Au spheres," where they occupy s states.

The two compounds closest to the compositional metal-insulator transition, KAu and RbAu, require only small volume changes in order to undergo a metal-insulator transition. An expansion corresponding to pressure of ≈ -30 kbar causes KAu to become a semiconductor. An experimental verification of this is, of course, not easy. RbAu is predicted to become conducting at a pressure of the order of 30 kbar.

The theoretical results which have been obtained could not be fully checked against experimental data. To the best of our knowledge, no measurements of heats of formation, bulk moduli, and metallization pressures have been published. Presumably, this is due to practical difficulties in sample preparation. Furthermore, the experimental studies of optical properties, in particular for RbAu and CsAu, are complicated⁴ by severe difficulties in the preparation of clean and stoichiometric sample surfaces.

*Permanent address: Laboratoire de Magnétisme et de Structure Electronique des Solides del' Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France.

†Physics Laboratory I, The Technical University of Denmark, DK-2800 Lyngby, Denmark.

‡Central Research Institute for Physics, P.O. Box 45, H-1525 Budapest, Hungary.

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