Connection between charge transfer and alloying core-level shifts based on density-functional calculations

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The measurement of alloying core-level binding energy (CLBE) shifts has been used to give a precise meaning to the fundamental concept of charge transfer. Here, ab-initio density-functional calculations for the intermetallic compound MgAu are used to investigate models which try to make a connection between the core levels shifts and charge transfer. The calculated CLBE shifts agree well with experiment, and permit an unambiguous separation into initial-state and screening contributions. Interestingly, the screening contribution is large and cannot be neglected in any reasonable description. Comparison of the calculated results with the predictions of simple models show that these models are not adequate to describe the realistic situation. On the positive side, the accuracy of the density-functional calculations indicates that the combination of experiments with such calculations is a powerful tool to investigate unknown systems.

71.50.+t, 78.65.Ez, 32.70.Jz

I. INTRODUCTION

The concept of charge transfer is fundamental to chemistry and condensed-matter physics. Unfortunately, it is frustratingly difficult to give a precise definition of charge transfer, or even a well-defined prescription for measuring it. This is equally true for related quantities such as electronegativity and bond ionicity.

There have been a number of attempts to relate the charge transfer in an alloy to the positions of the core levels. These energies can be measured with high accuracy using X-ray spectroscopy. In general terms, the core levels of an atom are shifted when the atom’s environment changes. Interesting cases are, for example, when a crystal is formed out of free atoms when an atom is at the surface rather than in the bulk of a solid, or when an alloy is formed out of two elemental solids.

In the case of the alloy core-level shift (the subject of this paper) a major objective has been to find a well-defined connection between the measured shift and the charge transfer between the constituents. Clearly, when charge is moved from one atom to another, an electrostatic potential builds up, which modifies the energy needed to eject an electron from a core level into the vacuum. In the simplest form of the “potential model”, the change of the potential felt by a core electron is described using a Madelung term and an on-site contribution. Unfortunately, cancellation between these effects and uncertainty in the model parameters make it difficult to extract reliable charge transfers using this approach.

Furthermore, the simple potential model is valid only for the “initial state” picture, i.e. when describing the positions of the core levels in the alloy and the pure metal before a core electron is removed. To compare with the measured binding energies, a final-state screening contribution must be taken into account: after a core hole is created, the remaining electrons relax to screen the hole. The kinetic energy of the emitted electron includes the screening energy. This can be included in the formalism (by a term generally denoted δR), but this adds another parameter whose numerical value is poorly known.

An alternative procedure is described in Ref. It was pointed out that the relaxation energy can be measured directly via the shift of the Auger parameter (the sum of core-level ionization and Auger-energy shifts). For the compounds AuMg and AuZn, the resulting values of δR are inconsistent with the estimates used in an earlier work based on the potential model, even though plausible ionicities were deduced there. A modified potential model was presented which relates the valence charge transfer in a metal to an atomic property, namely the change in the potential at the core due to changes in the valence and core occupation numbers.

Under these circumstances, it is desirable to make a detailed theoretical analysis of a typical system using a method which can quantify the various contributions unambiguously. Here we use ab-initio density-functional total-energy calculations to study the MgAu alloy. Using a supercell technique, the Mg, Au, and MgAu metals with and without a core hole on a selected atom can be described accurately. This cleanly separates the core-level shift into initial-state and final-state relaxation contributions, which can then be checked against the appropriate models. In addition, direct inspection of the densities of states, on-site charges, and screening charge distributions gives an understanding of the effects of alloying and the different screening responses to a core hole.

From the results, we are led to the conclusion that
the final-state relaxation contribution is not small, as it changes both the sign and the magnitude of the core-level shift on the Mg atom. This happens because the screening of the Mg 1s core hole is substantially less effective in the alloy than in the pure Mg metal. In contrast, the relaxation energy is found to be almost identical in the pure metal and the alloy for Au. By inspecting the screening density and comparing to free atom calculations, we try to offer a simple explanation for the changes in the screening properties upon alloying.

After obtaining a realistic picture of both the initial-state and the final-state screening terms, we have tried to interpret these results in terms of the potential model. However, is has not been possible to reproduce the features of the model. In brief, the potential model assumes the following connection between the shift $\Delta V$ in the core-level binding energy and the charge transfer $\Delta q$:

$$\Delta V = (k - M) \Delta q \quad (1)$$

where $k \Delta q$ is the on-site Coulombic potential and $-M \Delta q$ is a Madelung term from charges on the other lattice sites. Sometimes additional terms are included, e.g. in the form:

$$\Delta V = k \Delta q - M \Delta q - \delta R - e \delta \phi \quad . \quad (2)$$

where $-\delta R$ is the change in the final-state relaxation energy and $-\delta \phi$ is the change in the Fermi energy. Our calculations can supply reliable values for the well-defined quantity $\delta R$, but cannot assign values to poorly-defined quantities such as $\delta \phi$, $k$, and $M$. A substantial effort to recover the potential model in either formulation did not lead to any quantitative or even qualitative agreement.

II. CALCULATION AND INTERPRETATION OF CORE-LEVEL SHIFTS

Certain excitation energies (such as core-level shifts and atomic ionization energies) can be obtained as the difference of the total energies of two self-consistent density-functional calculations for the ground state. This can be done whenever the excited state is formally the ground state for a different set of quantum numbers. Although the calculated eigenvalues should not be directly associated with the excitation energies, a connection can be made using Slater’s transition state concept.

During an experiment such as XPS, an electron is emitted from the core state into the vacuum. The core-level binding energy is the difference of the total energies between the unperturbed, homogeneous crystal and the impurity system in which a single atom has a reduced core occupation. The first system is easy to handle using standard band-structure techniques, whereas the second requires some treatment suitable for impurities, such as use of supercells.

In a metal, a valence electron moves in from the surrounding crystal to screen the positive charge of the core hole. Effectively, the core electron has been lifted to the Fermi level hereby. The energy needed to do this can be expected to depend on the position of the core eigenvalue before the excitation and on the degree of screening of the core hole. The separation into “initial state” and “final-state screening” contributions can be made clearer using the transition-state concept. Within DFT, this is done using Janak’s formula which states that the derivative of the total energy respective to a some occupation number equals the corresponding eigenvalue. Applied to the present situation, the charge $x$ is taken from the core state of one atom in the supercell and put into the valence band, and

$$\frac{\partial E_T(x)}{\partial x} = E_F - E_c(x) \equiv \epsilon_c(x), \quad (3)$$

where $E_T$ is the total energy, $E_F$ is the Fermi energy, and $E_c$ is the core-level eigenvalue.

Actual calculations show that, to a very good approximation, the core eigenvalue drops in a nearly linear fashion as it is deoccupied, even though the overall core-level drop is substantial. For example, $\epsilon_c$ increases from 1248.6 to 1364.7 eV when the Mg 1s occupation is reduced from two to one. Similarly, the Au 4f state starts at 78.6 eV below the Fermi energy and drops to 93.3 eV.

Assuming a strictly linear dependence of $\epsilon_c$ on $x$, the core-level binding energy (the change in total energy when one electron is taken from the core) can be written in various illuminating ways:

$$E_T(1) - E_T(0) = \int_0^1 \epsilon_c(x) dx \quad (4)$$

$$\approx \epsilon_c(\frac{1}{2}) \quad (5)$$

$$\approx \frac{1}{2}[\epsilon_c(0) + \epsilon_c(1)] \quad (6)$$

$$\approx \epsilon_c(0) + \frac{1}{2}[\epsilon_c(1) - \epsilon_c(0)] \quad (7)$$

These equations express the full core-level binding energy (CLBE) including final-state relaxation effects in terms of the eigenvalues at different occupations. Eq. 2 is Slater’s transition-state rule, and Eq. 3 shows that the CLBE is the average of the eigenvalues before and after removing the core electron. In Eq. 4, the first term $\epsilon_c(0)$ is the initial-state CLBE and the relaxation contribution is identified as one-half of the core-eigenvalue drop upon depopulation.

This description is a useful tool to interpret the calculated results because it makes contact between core-level shifts and differences in the screening response. The core-level shift is the difference of the CLBE in two different environments, say $A$ and $B$. The initial-state core-level shift is the difference of the static core levels in the unperturbed systems. According to Eq. 2, the final-state relaxation contribution can be expressed as the difference of the core-eigenvalue drop upon depopulation. In general terms, a core level drops more strongly when the valence electrons screen the core hole less efficiently. Thus,
the initial-state picture for the core-level shift is applicable if the screening of the core hole is the same in both systems. If there is a positive relaxation contribution to the core-level shift from \( A \) to \( B \), this shows that the core-level drop is larger and the screening less effective in system \( B \). Conversely, a negative relaxation contribution indicates that screening is more effective in \( B \).

### III. CALCULATIONAL PROCEDURE

To determine the initial-state CLBE, a calculation for the unperturbed periodic systems is adequate. Hereby it is advantageous to use an all-electron method, which gives the core eigenvalues directly. For the complete CLBE including final-state relaxation, a supercell is used and the difference of the total energy with and without a core hole on one atom is evaluated. As discussed, the electron taken from the core state is placed into the valence band. For additional information, the promoted charge can take non-integer values. Within a self-consistent DFT calculation, the important screening effects should be described accurately. Note that the properties of the surface, specifically the work function, do not enter either description. This must be the case for an acceptable model since the true core binding energy relative to the Fermi level, expressed as the difference of two total energies, is a bulk property.

The electronic-structure and total-energy calculations presented here were done with the all-electron full-potential LMTO method [16] within the local approximation (LDA) to density-functional theory [17]. Minimization of the energy under a constrained core occupation is rigorously justified in the DFT framework: a self-consistent calculation under the chosen constraint provides a variational total energy in the parameter subspace identified by the constraint.

We applied this technique to the core levels of the Mg 1s and Au 4f levels, first for the pure materials and second for the binary MgAu alloy in the CsCl structure. Accurate experimental data exist on the core level shifts upon formation of this alloy. To make comparisons between the materials easier, the fcc structure was adopted for pure Mg. To study the core-hole–excited solids, we used 16-atom supercells for both CsCl-structure MgAu, and fcc Mg and Au. The distances of the core hole from its periodic images exceeds 12 bohr in all cases, and tests show that our values for the core level shifts are converged with respect to cell dimension. The localization of the calculated density response to the core-hole perturbation, as detailed below, provides an *a posteriori* justification for the used supercells. The Brillouin-zone integration was done using more than 50 irreducible special points. Muffin-tin radii for Mg respectively Au are 2.94 and 2.60 bohr in the pure metals and 2.50 and 2.70 in the compound at the experimental lattice constants, and are scaled with the lattice constant. All the calculations are scalar-relativistic and use the Vosko *et al.* parameterization of the LDA exchange-correlation potential [17].

### IV. RESULTS FOR MgAu

The calculated structural parameters for MgAu, Au and Mg are given in Table I. The results for these bulk systems are of standard DFT-LDA quality. For the calculation of the core holes, supercells were built up at the theoretical lattice constant.

Before moving to a discussion of the core level shifts, we point out that the absolute core binding energies in Table I (referred to \( E_F \), and obtained as total-energy differences) are in remarkable agreement with experiment, showing errors below 1%. The data in the Table also illustrates the large drop of the core eigenvalues when an electron is removed (about 14.5 eV for Au and 120 eV for Mg). By averaging the eigenvalues before and after removal of the core electron, Eq. I can be verified, showing that to a good approximation the core eigenvalue indeed drops linearly relative to the Fermi energy as charge is removed.

The calculated initial-state and full core-level shifts are obtained by taking the differences of the corresponding values in Table I, leading to the values shown in Table II and (graphically) in Fig. 1. The difference between the full and initial-state CLS then gives the screening contribution. The full results are in good agreement with experiment for both cases. We find that the initial-state estimate is already accurate for the Au 4f shift, but that it is grossly incorrect and even has the wrong sign for Mg 1s. The screening contribution to the shift is thus completely different for the two types of atom: it is negligible for Au, but is the dominant contribution for Mg. The screening energies are in reasonable agreement with those deduced from Auger parameter measurements, but are incompatible with the assumptions made in earlier work [18].

In view of the discussion in Section II, the conclusion is that the Au 4f core hole is screened equally well in the pure metal and in the alloy. For Mg, on the other hand, the depopulated 1s core level has dropped by a larger amount in the alloy, showing that the core hole is screened significantly less effectively there than in pure Mg. Given the size of the effect, an analysis of measured core level shifts which does not take screening into account is pointless.

The calculations reproduce the experimental core-level shifts and split these unambiguously into an initial-state and a final-state screening term. In the rest of this section, we discuss these contributions separately in view of the calculated electronic structure and the potential-type models. In the end, we will come to the conclusion that the potential models are difficult to justify on the basis of realistic calculations.

To help in the interpretation of the results, the site-
resolved densities of states are presented in Figs. 2, 3, and 4. Fig. 2 compares the electronic structure of Mg, Au, and MgAu before making a core hole. The effects of a Mg 1s or Au 4f core hole on the valence states of Mg and Au are shown in Fig. 3 those in MgAu in Fig. 4.

A. Initial-state shifts

The calculated initial-state core-level binding-energy (i-CLBE) shift upon alloying Mg and Au to form MgAu is $\Delta_{\text{Mg}} = -0.45 \text{ eV}$ for the Mg 1s state and $\Delta_{\text{Au}} = 0.71 \text{ eV}$ for the Au 4f state. A charge transfer of about 0.1–0.2 electrons from Mg to Au is generally considered reasonable, in view of the electronegativity values of 1.31 and 2.54 for Mg and Au, respectively. A reliable definition of the charge transfer (say, as charge density integral) from a density-functional calculation is very difficult to set up, so we will not try to verify the generally accepted value directly. However, we can inspect whether the calculated initial-state shift is compatible with the potential model for this accepted value of the charge transfer. We also discuss other modeling concepts which attempt to explain the initial-state CLBE shift. In the end, an honest appraisal is that no simple model can account for the calculated values, despite extensive efforts to find one.

As described above, the basic feature of the potential model is that a charge transfer to the atoms of type B causes a repulsive on-site Coulomb potential which pushes up the core states, reducing the (initial-state) CLBE. This effect is only partly compensated by the Madelung potential. Thus, the CLBE is reduced for those atoms which acquire additional charge, and vice versa. On the other hand, we can also present an equally simple alternative model, based on a rigid-band description, where this effect is reversed. Assume (with reference to Figs. 2, 3, and 5) that the density of states (DOS) of the alloy is obtained by adding together the two DOS of the constituents, shifted vertically to line up in some way which reflects the bonding. The charge on an atom in the alloy is then simply related to the position of the shared alloy Fermi energy with respect to the site-decomposed valence DOS. Furthermore, we assume that the core eigenvalues are at a fixed position relative to the valence band, so that the core levels track the shifts of the DOS. Since the CLBE is defined relative to the Fermi energy, it follows that charge transfer to sites of type B is associated with an upward shift of the Fermi energy and a larger initial-state CLBE.

In the case of MgAu, we are assuming that there is charge transfer from Mg to Au, and have calculated that there is an increase of the Au 4f CLBE in the alloy. The Mg atom has lost some charge by alloying and has a reduced CLBE. Even if only the signs are considered, these features are incompatible with the potential model, but agree with the rigid-band description. In fact, we can become ambitious and try use the calculated values of the density of states at the Fermi level for the pure Mg and Au materials ($D_F(Mg)=0.46 \text{ states/eV}$ and $D_F(Au)=0.33 \text{ states/eV}$) to connect the CLBE shifts with the charge transfer. Assuming a reasonably flat DOS at the Fermi energy, the transferred charge for an atom of a certain type is approximately equal to

$$\Delta q = D_F \Delta \epsilon_c$$

which yields $-0.21$ and $0.23$ electrons for Mg and Au, respectively. These values are close to the generally accepted charge transfer for this type of alloy; furthermore, the charge transferred away from Mg is close to the charge transferred to the Au atom.

Unfortunately, this gratifying result must be considered accidental, for several reasons. Foremost is that the alloy has a substantially smaller volume than the sum of the volumes of the constituents: the cell volumes are 113.3, 146.9, and 225.9 bohr$^3$ for Au, Mg, and MgAu, respectively. It makes sense to assign the shrinkage of 13% to the softer Mg atom. Thus, a more correct description could be to “prepare” the Mg atom by compressing it to a smaller volume, then forming the alloy from this compressed Mg and the Au crystal. The total i-CLBE shift then is a sum of the effects due to the two steps. Independent of whether the shrinkage is assigned to the Mg or Au atoms, we are now considering a simpler system in which an alloy is formed without any volume change. If the rigid-band model is a reasonable description, it should be equally applicable here. When the Mg bulk is compressed, the 1s core level moves up by 0.51 eV, reducing the CLBE from 1248.62 eV to $\epsilon_c=1248.11$ eV. This value is almost equal to that in the alloy, so that the estimated charge transfer for the Mg atom from the rigid-band model now comes out close to zero. Unfortunately, this is not compatible with the charge of 0.23 electrons added to the Au site, throwing the perceived success of the rigid-band model into doubt.

At this stage, it can be speculated that shifts of the Fermi energy should be included, arising from changes in the electronic structure due to alloying. Indeed, the plots of the DOS in Figs. 2 to 4 show that the rigid-band assumption is not conspicuously well satisfied. To demonstrate that all kinds of other effects of similar magnitude would still be neglected, we focus on just one aspect, namely the role of $sp$ to $d$ charge promotion during alloying. This can be most easily investigated in an ASA calculation, where the total crystal volume is assigned to atomic spheres. The ASA result for the initial-state CLBE shifts when alloying Mg$^t$ and Au reproduces the full-potential calculation reasonably well. The interpretation of the CLBE shift can now be given a new dimension, since we can directly investigate the response of the core eigenvalues to changes in the $sp$ and $d$ charges. We obtain response parameters $\partial \epsilon_c / \partial Q_f \approx 3 \text{ eV/electron}$ for the $sp$ and $\approx 1.5 \text{ eV/electron}$ for the $d$ states. Furthermore, we can inspect the changes in the partial charges $Q_f$ when the Mg atom is taken from the pure (compressed) Mg$^t$ crystal and is placed in the alloy, obtaining
\[ \Delta Q_{sp} \approx -0.21 \text{ and } \Delta Q_d \approx 0.28 \text{ electrons.} \] Thus, only 0.07 electrons are added to the Mg atomic sphere, but \( \approx 0.25 \text{ electrons are promoted from the } sp \text{ to the } d \text{ states.} \] Combined with the response parameters, it follows that a contribution to the initial-state CLBE shift of about \(-0.3 \text{ eV} \) should be attributed to the \( sp \text{ to } d \) promotion. Altogether, this shows that not only do the core states shift relative to the valence band when charge is transferred, but the effect is significantly different depending on the angular momentum which takes up the charge.

In sum, despite attempts in various directions, we have not been able to find a simple model which can describe the initial-state CLBE shifts caused by alloying. The simple potential model is not applicable because even the signs are not predicted correctly. The rigid-band model seems slightly more plausible, but also suffers from a number of shortcomings. Theoretically, an extended model could be written down which includes numerous other relevant effects, such as \( sp \)-to-\( d \) promotion etc. However, this model would be so complicated and unwieldy that the overall aim of a simple model would be negated. Having confidence in our calculations, we believe that the values of \(-0.45 \text{ eV} \) and \( 0.71 \text{ eV} \) for the \( 1\text{-CLBE} \) shift are reliable, but we have no convincing way to explain these numbers in simple terms.

### B. Final-state screening contribution

Next, we discuss the final-state screening contribution to the CLBE shifts when Mg and Au are alloyed to make ordered MgAu. As mentioned above, the calculated screening contribution is \( 0.02 \text{ eV} \) for Au and \( 0.70 \text{ eV} \) for Mg (Table 1). This was interpreted as follows: the screening of the Au \( 4f \) core hole happens in a way which is nearly independent of the environment. In contrast, the screening of the Mg \( 1s \) core hole is significantly different in the pure Mg bulk and in the alloy. More exactly, the core hole in the alloy is screened considerably less effectively than in pure Mg. In the following, we try to analyze this difference in the screening properties.

A major advantage of an accurate simulation such as a DFT calculation is that it can provide data which is not accessible to experiment; one example is the separation into initial-state and screening contributions. It is equally useful to use the calculation as a “microscope” to provide quantities such as the DOS or the charge density. In the present situation, we can develop a feeling for the nature of the core-hole screening by inspecting the screening density directly. This is simply the difference of the charge density with and without the core hole. One additional electron is in the valence charge, responding to the attractive core-hole potential. The electronic structure is similar to that of a Hg impurity in Au. In real space, the \( d \) states contract, although without any change in the occupation number. To the screening cloud, this process contributes the difference of the contracted and uncontracted \( d \) shell, which is a positive peak near the nucleus surrounded by a negative “ring.” At this stage, we have not yet taken up the extra screening electron. This is done by the \( sp \) states which now in turn screen (and fill in) the attractive ring. Since the \( sp \) states are more extended, this cannot be done completely, leaving some part of the negative ring visible in the total screening cloud.

For the quality of the screening, the charge closest to the nucleus is most relevant. On the Au atom this is dominated by the shrinking of the \( d \) shell, which can be expected to be largely independent of the environment. Screening by \( sp \) electrons is a more extended affair which can be influenced by the environment of the atom. However, for Au the \( sp \) electrons play a less immediate role, even though they actually take up the additional screening electron. In contrast, screening of the Mg \( 1s \) core hole is done only by \( sp \) valence electrons in the form of an extended cloud. Overall, these arguments can explain why screening is largely independent of the environment in Au but not in Mg, in agreement with the calculated results for the alloying process.

Next, we compare the screening of the core holes in the pure materials and the MgAu alloy. For the Au \( 4f \) core hole, the screening clouds in the density plots look very similar in the central \( d \)-electron lump, with some differences in the outer regions. Based on the discussion above, we can easily accept that the screening is similar in Au and MgAu and that only an insignificant contribution to the Au \( 4f \) CLBE shift is obtained. For the case of Mg, we wish to understand why the screening in the alloy is significantly less effective. Unfortunately, in this context it is again difficult to obtain a clear answer.

A first possible explanation for the less effective screening in the alloy is that charge has been transferred away from the Mg atom, leaving less charge to respond to the attractive core hole, leading to reduced screening. However, if we count the number of electrons inside a sphere of a fixed radius \( R_0 = 2.8 \text{ bohr} \) we find that the sphere
charge in the alloy is 0.36 electrons above that in pure Mg. This is presumably a consequence of the reduced volume in the alloy. Even though the additional charge is mainly in the outer regions of the sphere, it would seem to invalidate an explanation based on reduced available valence charge.

Secondly, a comparison of the DOS for pure Mg with the Mg site in MgAu shows that the single-metal parabolic sp DOS has changed to some degree of covalent character in the alloy, with a minimum of the DOS around −0.2 Ry. It can be speculated that this leads to a somewhat more rigid valence charge density, which cannot respond as flexibly to the core hole potential. This effect could play a role, but is not confirmed or invalidated by the calculation.

Finally, Fig.6 shows antiscreening features on the neighboring Au atoms. This could be interpreted as a “variable wavelength Friedel oscillation” whereby the Friedel wavelength changes from a value appropriate to Mg to a shorter one on the Au atoms. The antiscreening could push the first node of the screening density inwards with a corresponding reduction of the screening charge. This explanation, while potentially applicable, also cannot be confirmed unambiguously.

V. SUMMARY AND CONCLUSIONS

In this paper, we have presented the results of ab initio density-functional theory calculations of the core level shifts which arise upon alloying, using the prototypical intermetallic compound MgAu as an example. We were interested in the following questions: how well the experimental results can be reproduced; how the full core level shifts can be separated into initial-state and final state screening contributions; and whether the results can be understood in terms of simple models.

The agreement to experiment turns out to be good. The calculated core-level shifts are 0.73 and 0.25 eV for the Au 4f and Mg 1s states, respectively, close to the measured values of 0.74 and 0.34 eV. Given the complexity of the problem, these results are very satisfying. We have also found that the absolute core-level binding energies, calculated as the difference of two total energies, agree to within 1% with the experimental results.

The calculations give an unambiguous separation of each core level shift into a static initial-state contribution and a term due to the final-state screening of the core hole by the other electrons. Such a separation is central to all subsequent attempts to understand the results using simpler concepts. Somewhat unexpectedly, we find that the screening contribution is not just a small correction, but changes the picture drastically. Specifically, the shift of the Mg 1s core state changes sign when screening effects are included.

Extensive attempts were made to evaluate the calculated results in terms of simpler models. For the initial-state shifts, however, no convincing model could be found which is able to predict the calculated values. Among other considered descriptions, the well-known “simple potential model” could not be confirmed. The basic difficulty is that a large number of effects influence the core level binding energy. The situation is considerably too complicated to be cast into any simple model with only a few parameters. Possibly, a series of calculations for several different systems could uncover trends and help to formulate a better model, but we do not consider it plausible that an adequate general model can be found.

For the screening contribution, we have used the calculations to obtain accurate images of the screening clouds for the different cases. This information cannot be obtained from experiment and is of major help when trying to obtain insight into the nature of the screening process. Indeed, straightforward interpretations for the screening mechanism at the Mg and Au sites could be deduced. Whereas the screening of the Mg core hole is done by a relatively extended sp-electron cloud, screening in Au takes place in a two-step process. First, the full Au d shell contracts in response to the attractive core-hole potential, then the sp valence electrons fill up the depletion ring around the d shell. This description is in line with the result that the Mg screening depends on the environment, while Au screening does not.

Two conclusions are drawn from the results. First, while it is possible to obtain insight into the electronic structure changes upon alloying and the screening behaviour, simple models which try to connect the alloying core-level shifts with charge transfer cannot be confirmed. This is mainly due to the complexity of the real system which is not compatible with a description involving only a few quantities. Specifically, this means that charge transfer is only one of several quantities involved, and in fact one of the most poorly defined ones. Secondly, a full ab-initio calculation can reproduce measured core-level binding energies and their shifts to very good accuracy. This shows that simpler models are not actually needed in order to interpret measured values, where such measurements are used to investigate systems with unknown properties. Instead, density-functional calculations should be used for this purpose.

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| Case   | $\epsilon_c(0)$ | $\epsilon_c(1)$ | calc. | exp. |
|--------|------------------|-----------------|-------|------|
| Au 4f in Au | 78.64 | 93.25 | 85.78 | 85.88 |
| Au 4f in MgAu | 79.35 | 94.15 | 86.51 | 86.62 |
| Mg 1s in Mg | 1248.62 | 1364.74 | 1306.78 | 1303.20 |
| Mg 1s in MgAu | 1248.17 | 1365.35 | 1307.03 | 1303.54 |

TABLE II. Calculated and measured core-level binding energies in eV, referred to the Fermi energy. Column headings: “$\epsilon_c(0)$” and “$\epsilon_c(1)$” are the calculated eigenvalues before respectively after making the core hole; “calc” denotes the calculated CLBE as a total-energy difference; “exp” gives the experimental data from Ref. 8.

| Case   | initial | screening | full | exp. |
|--------|---------|-----------|------|------|
| Au 4f | 0.71    | 0.02      | 0.73 | 0.74 |
| Mg 1s | −0.45   | 0.70      | 0.25 | 0.34 |

TABLE III. Mg 1s and Au 4f core-level shifts in the MgAu alloy with respect to pure Au and Mg in eV. Column “initial” is the initial-state shift, “screening” is the final-state screening contribution, “full” is the full calculation, “exp” is the experimental data from Ref. 8.

| Case   | $a_0$ (bohr) | $B_0$ (Mbar) |
|--------|--------------|--------------|
| MgAu th. | 6.09         | 1.05         |
| MgAu exp. | 6.15         |              |
| Au th.   | 7.68         | 1.85         |
| Au exp.  | 7.70         | 1.75         |
| Mg th.   | 8.38         | 0.40         |
| Mg exp.  | 8.46         |              |

TABLE I. Equilibrium lattice constant and bulk modulus for MgAu (CsCl structure), Au (fcc) and Mg (fcc). The experimental Mg lattice constant corresponds to the measured volume per atom in the hcp structure.
FIG. 1. Graphical representation of the calculated and measured core-level binding energy shifts in Table III. The full calculated result in column “Total” is decomposed into the initial-state and screening contributions. Note that the screening contribution on the Mg atom drastically changes the picture.

FIG. 2. Calculated site-resolved density of states for Mg, Au, and MgAu.

FIG. 3. Calculated site-resolved density of states for Mg and Au with, respectively, a Mg 1s or Au 4f core hole. Mg* or Au* denotes the site with the core hole, and 1nn and 2nn are the first and second-nearest-neighbor sites, respectively.
FIG. 4. Calculated site-resolved density of states for MgAu with a Mg 1s or Au 4f core hole. Details as in Fig. 3.

FIG. 5. Screening charge density for a 1s core hole at the Mg site in fcc Mg. Contour spacing ±5, ±15,... times $10^{-3}$ bohr$^{-3}$. The solid and dashed lines show positive and negative densities, respectively.

FIG. 6. Screening charge density for a 4f core hole at the Au site in fcc Au. Details as in Fig. 3.
FIG. 7. Screening charge density for a 1s core hole at the Mg site in MgAu. Details as in Fig. 5.

FIG. 8. Screening charge density for a 4f core hole at the Au site in MgAu. Details as in Fig. 5.