ceptibilities have similar power spectra. This is *not* the case when fluctuations take place between magnetic and nonmagnetic configurations. Pressure or alloying often changes the average occupation of the $4f$ shell without destroying completely the homogeneity of the system. This implies changes in the parameters Δ and Γ of the model and can provide direct tests of the theory presented here. Implicit in the one-impurity treatment of the problem is the prediction that the inelastic peak is a feature that does not depend on concentration of Tm sites and should also appear in dilute systems.

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Electron Transfer and the Valence States of Cerium and Platinum in Cubic Friauf-Laves Compounds with the Platinum Metals

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An analysis of the observed values of the lattice constants of the crystalline solutions $CeIr_2$-$CePt_2$ and other Friauf-Laves intermetallic compounds leads to the conclusion that at 14 at.% $CePt_2$ in $CeIr_2$ the platinum atom has transferred one electron to cerium and forms nine covalent bonds in pivoting resonance, without having a metallic orbital, whereas in $LaPt_2$ and $CePt_2$ it has 0.72 metallic orbital, an unshared electron pair, and covalence 7.28. The choice of valence states 3^+ and 4^+ of cerium in different compounds is also discussed.

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Barberis *et al.*[1] have determined the values of the lattice constant (cube edge) for the crystalline solutions $CeOs_2$-$CeIr_2$ and $CeIr_2$-$CePt_2$, which have the Friauf-Laves cubic structures $C15$, and have interpreted the values, in comparison with those for the compounds $LaOs_2$, $LaIr_2$, $LaPt_2$, $PrOs_2$, $PrIr_2$, and $PrPt_2$, as showing that the cerium atom is present as the tetrapositive ion in the compounds with osmium and iridium and the tripositive ion in the compound with platinum. Values of the lattice constants are shown in Fig. 1. There is a striking feature shown in this figure: the sharp bend in the $CeOs_2$-$CeIr_2$-$CePt_2$ curve at $Ce(Ir_{0.87}Pt_{0.13})_2$. I point out that this feature can be explained by application of known structural principles.

In the elemental metals Re, Os, Ir, Pt, and Au, with the atoms arranged in cubic or hexagonal closest packing, the observed interatomic distances (average of two for hcp) have a minimum about 30% of the way between Os and Ir; that is, for 8.3 valence electrons (electrons outside the xenon closed shell), as is shown in Fig. 2. This observation, which applies also to the sequence Tc, Ru, Rh, Pd, and Ag, has been interpreted[3] in terms of the 0.72 orbital, called the metallic orbital, that serves a special function in conferring metallic properties on metals.[4,5]

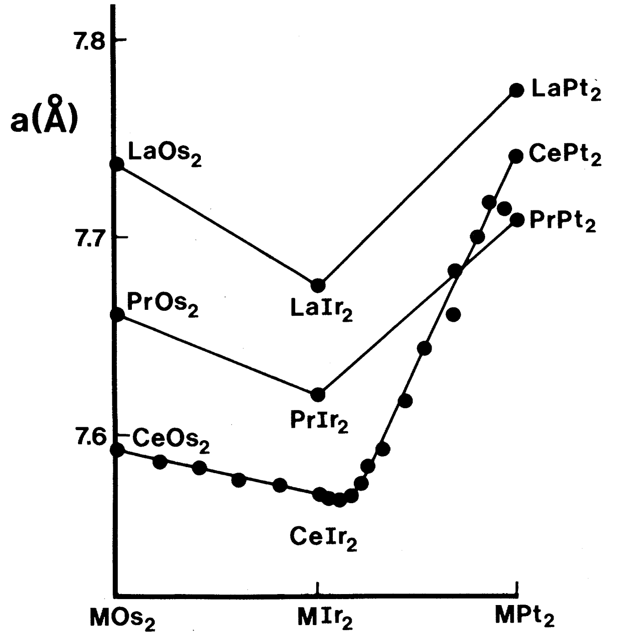

FIG. 1. Values of the lattice constant (edge of unit cube) of some Friauf-Laves intermetallic compounds and crystalline solutions, from Refs. 1 and 2. Note the bend at about $Ce(Ir_{0.87}Pt_{0.13})_2$.

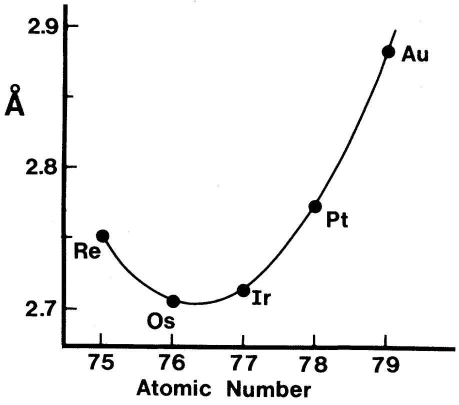

FIG. 2. The observed values of interatomic distances in the closest-packed structures of the metals from Re to Au, showing the minimum at about 8.3 electrons beyond the closed-shell number 68.

Of the nine d^5sp^3 orbitals of a transition metal the remaining 8.28 are available for occupancy by bonding electrons (in the iron-group metals) or unshared electron pairs. The value 0.72 for the number of metallic orbitals per atom was originally derived from the shape of the curve showing the dependence of the value of the saturation ferromagnetic moment of the iron-group transition metals and their alloys with one another on the number of electrons beyond the eighteen of the argon shell.[4] In these metals each atom is surrounded by other atoms in number greater than its covalence (the number of electrons involved in the formation of shared-electron-pair bonds). If the covalence of each atom were just equal to the number of its bond orbitals the bonds could resonate among the available atom-atom positions only synchronously; for example, in a four-membered ring resonance could occur between the structures

$$\begin{array}{cc} M & M \\ | & | \\ M & M \end{array} \text{ and } \begin{array}{c} M\text{—}M \\ \\ M\text{—}M \end{array} .$$

Such a structure would not lead to metallic conduction. If, however, an atom has an additional orbital unsynchronized, resonance of single bonds can occur, such as

$$\begin{array}{cc} M & M \\ | & | \\ M & M \end{array} \text{ to } \begin{array}{ccc} M & \text{—} & M^- \\ & & | \\ M^+ & & M \end{array} .$$

The atom M^-, with covalence increased by one and with one more electron than the neutral atom, now has its formerly vacant metallic orbital occupied by an electron. Because of the small electron affinity of a negatively charged atom, M^- cannot accept another bond and hence does not need another vacant orbital, whereas M and M^+ do need the metallic orbital. Simple statistical considerations of the unsynchronized response of bonds indicate that about 25% of the atoms are M^-, 25% are M^+, and 50% are M, so that an average of 0.75 metallic orbitals per atom would be expected, in reasonable agreement with the empirical value 0.72. It is seen from the above discussion that with this sort of resonance the maximum average covalence cannot be greater than 0.72 less than the number of orbitals per atom—the 0.72 metallic orbital is effectively unoccupied. (One might say that there are metallic orbitals in number 1 per atom, but that they are occupied to the extent of 28%, leading to 0.72 unoccupied.)

The many resonance structures, involving motion of electrons from atom to atom, combine to give the levels of the energy bonds of the ordinary electronic theory of metals and provide an explanation of electronic conductivity and other metallic properties. One might say that the electric conductivity results from the motion of the positive charges of the M^+ and the negative charges of the M^- from atom to atom as the bonds resonate.

It may be hard at first to accept the idea that the p orbitals are involved in the bonding of the transition metals—in most of the conventional treatments these orbitals are ignored as involving too much promotion energy for electrons to occupy them. I have pointed out, however, that the same objection might be raised to promoting an electron from s to p in the atoms in diamond, germanium, and grey tin. The normal state of these atoms is $s^2p^2\,{}^3P$, with one p orbital unoccupied, but almost all treatments of the electronic structure of the crystals are based on the configuration sp^3, with one electron promoted from s to p with a promotion energy comparable in magnitude to that for the transition metals. The promotion energy is in all these cases provided by the increased bond energy of the additional bonds that are permitted by the promotion.

In compounds of elements with different electronegativity the covalent bonds have some ionic character, as determined by the difference in electronegativity of the atoms connected by the covalent bond.[6] This ionic character confers electric charges on the atoms.[7] The ionic character may be thought of as resulting from rapid resonance, for each shared-electron-pair bond, between an extreme covalent bond, defined as having one electron on each of the two bonded atoms, and the extreme ionic bond A^+B^-, with the two electrons occupying the atomic bond orbital of the more electronegative of the two atoms.[6,7] Values of the electronegativity of atoms have been assigned in various ways, mainly empirical, in particular from the analysis of bond-energy values[6,7] (values of the enthalpy of chemical reactions involving only single bonds). A partially theoretical but largely empirical equation relating the partial ionic character (amounts of the resultant positive and negative charges conferred on the unlike atoms connected by the covalent bond) of two atoms A and B and the difference in the electronegativity x_A and x_B of the two atoms has been formulated; it is

$$\text{Amount of ionic character} = 1 - \exp[(x_A - x_B)^2/4]. \tag{1}$$

In some instances, including intermetallic compounds and other alloys, these charges are decreased by a transfer of electrons in the opposite direction, especially from a hyperelectronic element (on the right side of the periodic table), which increases its valence by losing electrons, to a hypoelectronic element (on the left side), which increases its valence by adding electrons.[8] I may point out that these electron transfers may be described as permanent; they are not associated with the electrical conductivity, which results from the resonance of bonds among the available positions, with use of the metallic orbital, and in fact they occur in nonconducting as well as in conducting solids.

The number of electrons transferred is approximately the number required to neutralize the effect of the partial ionic character of the bonds in accordance with the principle of electroneutrality.[9] The principle states that in stable molecules or crystals the resultant electric charge on each atom is close to zero, and always between the limits -1 and $+1$.

In the treatment of the Friauf-Laves compounds I apply rigorously the following rules. (1) If the total number of valence electrons is not changed by the electron transfer (as between two hypoelectronic elements or between two hyperelectronic elements) the amount of electron transfer is that which neutralizes the effect of the partial ionic character of the bonds, bringing the resultant electric charges of all atoms to zero. (2) If the number of valence electrons is increased by the electron transfer this transfer occurs to the limit set by the number of available orbitals or by the electroneutrality principle (allowed resultant charge between -1 and $+1$).

The nature of the Friauf-Laves compounds.—In the $C15$ crystal $\mathrm{LaOs_2}$ each La atom has four La neighbors at 3.350 Å and twelve Os neighbors at 3.208 Å; each Os atom has six La neighbors at 3.208 Å and six Os neighbors at 2.735 Å.[2] The ratios of these bond lengths are fixed by the structure: the bond lengths are, respectively, $0.4430a$, $0.4156a$, and $0.3536a$. This constitutes a problem, in that the lanthanum atom seems to be crowded. The La-La distance in elemental lanthanum is 3.745 Å, and the Os-Os distances in elemental osmium are 2.675 and 2.735 Å, average 2.705 Å. In the $\mathrm{LaOs_2}$ crystal the Os-Os distance and the La-Os distance agree reasonably well with the values for the elements, but the La-La distance is much shorter, and, moreover, the lanthanum atom has sixteen neighbors, rather than twelve. Even if the six Os-Os bonds formed by each octacovalent osmium atom were to be assigned the bond number 1, the remaining covalence 2 would require the lanthanum atom to have covalence 4 (plus the amount involved in its four La-La bonds), which is greater than the number of its valence electrons, 3. This difficulty is resolved by the transfer of electrons from osmium to lanthanum. Such a transfer is, moreover, indicated by the fact that lanthanum is much less electronegative than osmium.

The values of the electronegativity[7] of La, Ce, and Pr are all 1.0 and those of Os, Ir, and Pt are all 2.2. The difference, 1.2, corresponds by Eq. (1) to 30% ionic character of the bonds (La, Ce, Pr)—(Os, Ir, Pt). Both La, with three valence electrons, and Os, with eight are hypoelectronic, so that rule 1 applies. I assume, as an approximation, that the valence of lanthanum atom is equally divided among the sixteen bonds that it forms (four to La and twelve to Os). Let v be the valence of La after the electron transfer. The number of its shared-electron-pair bonds to Os is then $\frac{3}{4}v$, and, with 30% ionic character, the number of electrons transferred from La by this ionic character is $0.3\times\frac{3}{4}v$. The number of electrons transferred to La is $v-3$. Equating this, to achieve zero resultant charge, leads to $v=3.87$ for La, which corresponds to $v=7.56$ for Os, the total valence for $LaOs_2$ being 19.

For $LaIr_2$ we recognize that Ir is a hyperelectronic element, because the number of its outer electrons, 9, is greater than the number of available orbitals, 8.28. By rule 2 we expect the transfer of 0.72 electrons from each Ir atom to La, providing Ir with the maximum value permitted by the retention of 0.72 metallic orbitals and leading to valences 4.44 for La and 5.28 for Ir, with total 21. The resultant electric charges, -0.44 on La and $+0.22$ on Ir, are compatible with the electroneutrality rule.

In $LaPt_2$ the Pt atom has ten outer electrons. To achieve the valence 8.28 (retaining the 0.72 metallic orbital) would require the transfer of 1.72 electrons from each of two Pt atoms to the La atom. Such a transfer would place the resultant charge -1.99 on La, and it accordingly is ruled out by the electroneutrality principle. The alternative is that Pt retain an unshared electron pair in one of its *spd* orbitals, transfer 0.72 electrons to La, and achieve the valence 7.28, the total valence for $LaPt_2$ then being 19.

These considerations account for the course of the lattice constant a in the sequence $LaOs_2$-$LaIr_2$-$LaPt_2$. From $LaOs_2$ to $LaIr_2$ the single-bond radius of the transition metal[10] decreases by 0.01 Å and the number of bonding electrons increases by 10.5% (from 19 to 21), both changes having the effect of decreasing a. From $LaOs_2$ to $LaPt_2$ the number of bonding electrons does not change but the single-bond radius of the transition metal increases because of the unshared pair on Pt, and this leads to the increase in a. The increase in a is by 0.48%, which is compatible with the observed effect of an unshared electron pair on the single-bond radius in the elemental metals.

The $CeIr_2$-$CePt_2$ alloys.—From Fig. 1 we see that, whereas the $CeOs_2$-$CeIr_2$ alloys conform to Vegard's law that the lattice constant is linear in the mole fractions of the components, the $CeIr_2$-$CePt_2$ alloys do not. Up to about 13 at.% $CePt_2$ the values of a lie on a continuation of the $CeOs_2$-$CeIr_2$ curve. We know that some atoms in an alloy can have a structure involving the maximum covalence, dispensing with the metallic orbital. An example is the carbon atom in cementite, Fe_3C. For such an atom there occurs pivoting resonance of the bonds connecting it with its neighbors, which themselves have the metallic orbital (that is, 0.72 orbital). A platinum atom could lose one of its valence electrons, but not more, because of the limit placed on its charges by the electroneutrality principle. With no metallic orbital, its valence would then be 9. It could be surrounded by six Ir neighbors, each of which could lose 0.72 electrons to cerium, in order to free their metallic orbitals. The $Pt^{+1}Ir_6{}^{+0.72}$ complex would thus transfer 1.52 electrons to each cerium atom. The partial ionic character of the bonds would bring the resultant charges of all the atoms close to zero.

The maximum amount of $CePt_2$ allowed by this structure corresponds to the presence of $PtIr_6$ groups; that is, to mole fraction $\frac{1}{7}=0.14$ of $CePt_2$, in agreement with the observation that the bend in the lattice-constant curve occurs at this composition, $Ce_7Pt_2Ir_{12}$. There is the possibility that a superstructure could be detected in this alloy, probably with rhombohedral symmetry.

The lattice constants for the alloys between $Ce_7Pt_2Ir_{12}$, containing Ce^{4+} and enneacovalent platinum, and $CePt_2$, containing Ce^{3+} and platinum with covalence 7.28 after electron transfer, as discussed above for $LrPt_2$, conform to Vegard's law.

The platinum atom is not unique in having a different valence and different size in solution in low concentration in another metal and in the pure substance. Other examples have been discussed by Pauling and Pauling.[11] An increase in valence is usually caused by the need to fit into a smaller hole.

The valence of cerium.—The usual oxidation state of cerium is the tripositive state, Ce^{3+}, with Ce^{4+} less common. In a standard chemical reference book there are listed thirty Ce^{3+} compounds and ten Ce^{4+} compounds. In the elemental metal the metallic valence is indicated by the observed bond length to be 3.2; a denser modification with valence approaching 4 has been observed to form at low temperature[12] and at high pressure.[13] We may accordingly ask why in $CeOs_2$ and $CeIr_2$, but not in $CePt_2$, the cerium atom is in the Ce^{4+} state. Several factors may be involved, with the most important one the ratio of the effective covalent radii. The effective radius of Ce^{4+} is about 0.10 Å less than that of Ce^{3+}, and accordingly Ce^{4+} would be expected in crystals with the transition metals of smaller radius.

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