VOLUME 72, NUMBER 15 PHYSICAL REVIEW LETTERS 11 APRIL 1994

From Hexagonal Close Packed to Rhombohedral Structure: Relativistic Effects in Zn, Cd, and Hg

Prabhakar P. Singh
Department of Chemistry and Materials Science, L-268, Lawrence Livermore National Laboratory, Livermore, California 94550

(Received 29 November 1993)

We study the effects of relativity on the stability of group II elements Zn, Cd, and Hg in face-centered cubic (fcc) and hexagonal close-packed (hcp) structures. A comparison of nonrelativistic and scalar-relativistic results for both the fcc and the hcp phases of these elements, obtained self-consistently, clearly shows that the change in the most stable crystal structure from the hcp to the fcc-like rhombohedral, as one goes from Zn to Hg, is due to relativity. The stability of different structures is explained in terms of the increase in *s*-*p* hybridization resulting from relativity.

PACS numbers: 71.10.+x, 71.20.Cf, 72.15.Eb, 71.55.−i

Many electronic properties of simple metals such as Be, Mg, Zn, Cd, and Hg are similar because of their closed *s*-shell atomic configuration, ns^2. The similarity in the electronic structure of group II elements is also reflected in the fact that all of them have hexagonal close-packed (hcp) structure as their ground states except for Hg, which has a rhombohedral structure (at ambient temperature). The electronic origin of the change in the most stable structure from the hcp to the rhombohedral, as one goes from Be to Hg, is not obvious.

The apparent anomaly exhibited by the crystal structure of Hg *vis-á-vis* other divalent simple metals cannot be attributed entirely to the presence of 5*d* electrons because Zn and Cd also have 3*d* and 4*d* electrons, respectively, close to their *s* levels. However, we know that although atomic Hg has a closed *s*-shell configuration ($5d^{10}6s^2$) similar to other group II elements, the electronic structure of atomic [1] as well as bulk Hg [2, 3] depends critically on relativity due to its high atomic number. As the importance of relativity increases with increasing atomic number, it is possible that the apparent anomaly exhibited by the crystal structure of bulk Hg may have a relativistic origin.

The relativistic effects on the electronic structure of *atomic* Zn, Cd, and Hg are well documented [1], whereas earlier theoretical studies [2] of these effects on the band structure of *bulk* Hg are based on non-self-consistent charge densities and the treatment of 5*d* electrons as core electrons. In a recent work [3] we have studied the effects of relativity on bulk Hg using charge self-consistent calculations that treated 5*d* electrons as valencelike and thus allowed the 5*d* bands to hybridize with the 6*s*-6*p* bands. But the calculations reported so far were confined to face-centered cubic (fcc) or fcc-like rhombohedral geometry, and they did not examine the energetics of different structures. Also, it appears that there has been no systematic study of relativistic effects in Zn, Cd, and Hg, although such a study can be helpful in explaining the change in stable crystal structure from the hcp to the rhombohedral as one goes from Zn to Hg. The present study is intended to improve our understanding of the electronic structure of group II elements and provide some explanations for the stability of bulk Hg in the rhombohedral structure.

In this Letter we examine the effects of including the relativistic terms, the so-called mass-velocity and Darwin terms, on the electronic structure of Zn, Cd, and Hg in both fcc and hcp structures by carrying out charge self-consistent calculations using the linear muffin-tin orbital (LMTO) method in the atomic-sphere approximation (ASA) [4, 5], including the combined correction (CC) terms [4]. The calculations are carried out with the nonrelativistic Schrödinger equation as well as with the scalar-relativistic Dirac equation. We also consider 3*d*, 4*d*, and 5*d* electrons of Zn, Cd, and Hg, respectively, to be valencelike and thus allow the $(n-1)d$ bands to hybridize with the *ns*-*np* bands.

Based on our calculations, described below, we find that (i) relativity makes the fcc phase of Hg more stable than the hcp phase, (ii) the nonrelativistic calculations stabilize the hcp phases of Zn, Cd, and Hg, and (iii) the stability of different phases is determined by the change in *s*-*p* hybridization due to relativity.

The nonrelativistic (NR) and the scalar-relativistic (SR) self-consistent electronic structure of hcp and fcc Zn, Cd, and Hg are calculated with the LMTO method, including the CC terms. The **k**-space integrations are carried out with 256 and 456 **k** points in the irreducible wedges of the Brillouin zones of the fcc and the hcp structures, respectively. The exchange-correlation potential is parametrized as suggested by von Barth and Hedin [6]. To minimize the ASA-related errors in our calculations we do not introduce symmetry lowering relaxations, i.e., (i) for the hcp structure we use the ideal c/a ratio, and (ii) for the fcc-like rhombohedral structure we keep the angle between the axes, α, fixed at its fcc value.

The most important results of our calculations are shown in Fig. 1, where we show the difference in the equilibrium total energies between the hcp and the fcc structures for NR as well as SR cases,

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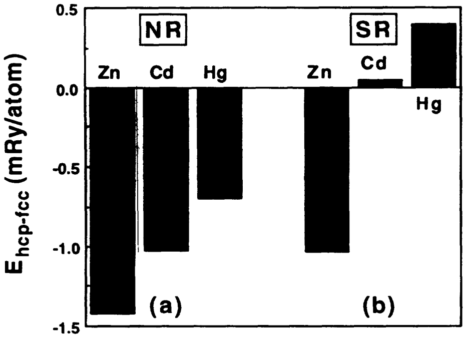

FIG. 1. The total energy difference between the hcp and the fcc phases of Zn, Cd, and Hg obtained with the LMTO method (a) nonrelativistically and (b) scalar relativistically.

$$\Delta E_{\text{hcp-fcc}} = E^{\text{total}}_{\text{hcp}} - E^{\text{total}}_{\text{fcc}} . \qquad (1)$$

In Eq. (1), $E^{\text{total}}_{\text{hcp(fcc)}}$ is the total energy per atom of the hcp (fcc) solid calculated with the LMTO method, including the CC terms. A positive (negative) $\Delta E_{\text{hcp-fcc}}$ indicates that the fcc (hcp) phase is more stable than the hcp (fcc) phase. The NR structural energy difference, shown in Fig. 1(a), clearly demonstrates that without relativity Zn, Cd, and Hg prefer the hcp structure over the fcc structure. Although NR $\Delta E_{\text{hcp-fcc}}$ decreases as one goes from Zn to Hg, the nonrelativistic hcp Hg is still quite stable, by −0.7 mRy/atom, in comparison with the nonrelativistic fcc Hg.

The inclusion of relativity changes the structural energy differences quite dramatically as can be seen from Fig. 1(b). Since the relativistic effects on Zn are expected to be minimal, it is not surprising to find the scalar-relativistic hcp Zn to be more stable than the fcc Zn, although $\Delta E^{\text{Zn}}_{\text{hcp-fcc}}$ has changed from its NR value of −1.42 mRy/atom to −1.03 mRy/atom. Within the accuracy of our calculations the total energies of SR Cd in the fcc and the hcp phases indicate that the two phases are essentially degenerate. Based on our calculations, in the following we argue that the hcp Cd should be more stable than the fcc Cd, in spite of the fact that the calculated total energies indicate the two structures to be degenerate. However, for SR Hg we find that the fcc phase is more stable than the hcp phase by 0.4 mRy/atom, as shown in Fig. 1(b). Thus *the change in the most stable crystal structure from the hcp to fcc-like rhombohedral structure, as one goes from Zn to Hg, is due to relativity.*

In order to understand the stability of different phases of Zn, Cd, and Hg, it is instructive to consider the effects that relativity has on the electronic structure of Hg. We know that the most dominant effect of relativity is to lower the s potential, which in turn can induce substantial s-d hybridization leading to electron transfer from $d \to s$ [7, 8]. Thus the amount of s-d hybridization can be significantly different between NR and SR results, but within the scalar-relativistic framework the localized nature of the d electrons ensures that the s-d hybridization as well as the electron transfer from $d \to s$ cannot be greatly affected by a simple rearrangement of Hg atoms. It suggests that the stability of SR Hg in the fcc phase rather than in the hcp phase, with both the fcc and the hcp structures having identical atomic arrangements up to second nearest neighbors (the difference being in the stacking sequence of $\{111\}$ planes only), is not due to the change in the s-d hybridization. On the other hand, the lowering of s potential also changes the s-p hybridization and the electron transfer from $s \to p$, and a simple rearrangement of atoms can significantly affect the spatially extended s electrons, which in turn can substantially change the s-p hybridization and the electron transfer from $s \to p$. Indeed, a comparison of our results for the fcc and the hcp phases for both NR and SR Zn, Cd, and Hg reveal that the change in electron transfer from $d \to s$ (≈ 0.003 electrons) due to change in structure is an order of magnitude smaller than the electron transfer from $s \to p$ (≈ 0.035 electrons).

Now the stability of different phases of NR and SR Zn, Cd, and Hg can be understood in terms of increase in s-p hybridization. The increase in s-p hybridization makes the electronic charge distribution more "covalent-like," thereby enhancing stability. The change in s-p hybridization in $(n-1)d^{10}ns^2$ metals, Zn, Cd, and Hg, can be measured in terms of the number of p-like electrons in these metals. Thus *an increase (decrease) in the number of p electrons as one goes from the fcc phase to hcp phase would indicate that the hcp phase is more (less) stable than the fcc phase.*

To show that NR calculations of Zn, Cd, and Hg lead to increased s-p hybridization as one goes from the fcc to the hcp phases, we plot in Fig. 2(a) the corresponding number of s and p electrons in these metals. Figure 2(a) shows that the number of p electrons in the hcp phases of NR Zn, Cd, and Hg is consistently larger than the corresponding values in the fcc phases, which indicates the stability of the hcp phases.

Since relativistic effects become more important for heavier elements, we expect the s-p hybridization in Zn to be affected the least among the three elements. Accordingly, we find that the scalar-relativistic hcp Zn is still more stable than the fcc Zn, as evidenced by the number of p electrons in the hcp Zn shown in Fig. 2(b). Similar analysis for SR Cd clearly suggests that the hcp Cd should be more stable than the fcc Cd, in agreement with the experimentally observed ground state. The structural energy difference, shown in Fig. 1(b), however, indicates that in the case of Cd the two structures, fcc and hcp, have essentially the same energy. Based on the fact that the self-consistent ASA potential, which determines the s-p hybridization, is quite accurate (i.e., close to the potential obtained with no-shape approximation [9]), we think that a more accurate total energy functional than the one used in our calculations, such as ASA + muffin-tin correction [10], would show the hcp Cd to be more

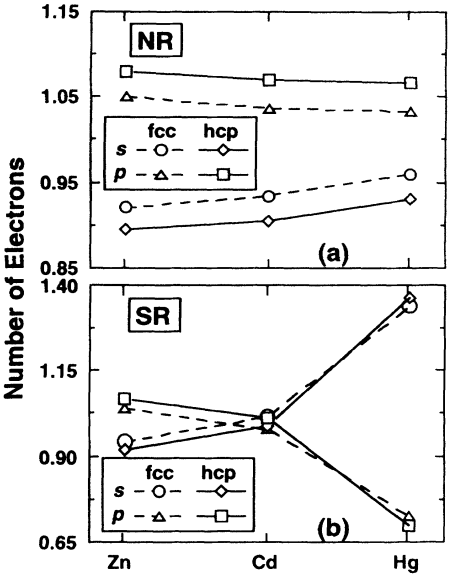

FIG. 2. The number of s and p electrons in the fcc and the hcp phases of Zn, Cd, and Hg obtained with the LMTO method (a) nonrelativistically and (b) scalar relativistically.

stable than the fcc Cd. Within the ASA approach one can also use the local-force theorem to obtain reliable structural energy differences [11]. In the case of SR Hg the number of p electrons in the fcc phase is larger than in the hcp phase, which confirms the stability of the fcc phase over the hcp phase. As shown in Fig. 2 the substantial increase in the number of s electrons for SR Hg is due to the deepening of the s potential, and the subsequent electron transfer from $d \rightarrow s$.

Further insight into the effects of relativity in Zn, Cd, and Hg can be obtained by examining the changes in the individual terms that make up the electronic charge density, $\rho(\mathbf{r})$, given by [12, 13]

$$\rho(\mathbf{r}) = \sum_{RL,R'L'} \chi^{\beta}_{RL}(\mathbf{r}_R)\, n^{\beta}_{RL,R'L'}(E)\, \chi^{\beta,*}_{R'L'}(\mathbf{r}_R)\,, \quad (2)$$

where $\chi^{\beta}_{RL}(\mathbf{r}_R)$, $n^{\beta}_{RL,R'L'}(E)$, R, and L are the LMTOs, the density matrix, site, and angular momentum indices, respectively. The superscript β denotes the most-localized tight-binding (TB) representation of Ref. [12].

In Fig. 3 we show NR and SR s-TB LMTO in the $z = 0$ plane of the hcp Zn and the fcc Hg calculated at their respective equilibrium lattice constants. Because of the contributions coming from the neighboring sites the orbital is spherical only close to its own site. A comparison of Figs. 3(a) and 3(b) shows that the changes in the s-TB LMTO of the hcp Zn due to relativity are confined well inside the atomic sphere, while changes outside the atomic sphere are very small. These changes are, however, responsible for bringing about $\approx 0.8\%$ contraction in the lattice constant of the hcp Zn as shown in Table I, where we compare the calculated equilibrium lattice constants and the bulk moduli of Zn, Cd, and Hg with the experimental values. In the case of the fcc Hg, relativity introduces changes not only well inside the atomic sphere but also outside of the atomic sphere, which result in more than 2% decrease in the lattice constant of fcc Hg. It is interesting to note that the lattice constant changes by only 1.2% in the hcp Hg.

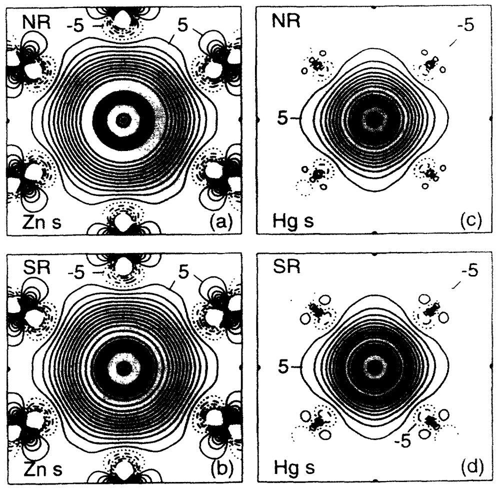

FIG. 3. The s-TB LMTO of hcp Zn and fcc Hg in the $z = 0$ plane calculated nonrelativistically [(a) and (c)] and scalar relativistically [(b) and (d)] at their respective equilibrium lattice constants. The negative-value contours are indicated by the dotted, dashed, dot-dashed, triple-dot-dashed, and long dashed lines with values corresponding to -5, -15, -25, -35, and -45, respectively, while the positive-value contours are denoted by solid lines at an interval of 10. All values have been multiplied by 10^3.

The relativistic changes in the densities of states (DOS) of the fcc as well as the hcp Zn and Hg are shown in Fig. 4. As expected, the effect of relativity on Zn is

TABLE I. The nonrelativistic (NR) and the scalar relativistic (SR) equilibrium lattice constants a (in atomic units) and the bulk moduli B (in Mbar) for the fcc and the hcp phases of Zn, Cd, and Hg calculated with the LMTO method, including the combined correction terms. The experimental lattice constants and the bulk moduli are also given. The numbers in parentheses are the experimental values of c/a for hcp Zn and Cd, and the angle between the axes α for rhombohedral Hg.

		NR		SR		
		fcc	hcp	fcc	hcp	Expt.
Zn	a	7.239	5.095	7.180	5.053	5.028 (1.856)
	B	0.96	0.50	1.02	0.52	0.598
Cd	a	8.309	5.848	8.176	5.761	5.633 (1.886)
	B	0.63	0.33	0.71	0.36	0.467
Hg	a	8.680	6.112	8.503	6.039	5.652 (70°45')
	B	0.65	0.33	0.48	0.21	0.382

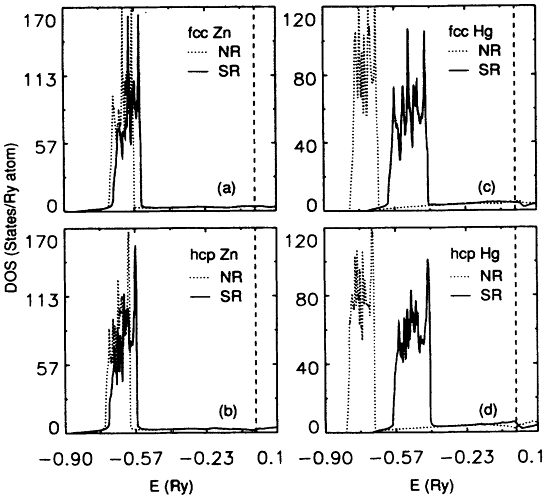

FIG. 4. The nonrelativistic and the scalar relativistic total densities of states of Zn [(a) and (b)] and Hg [(c) and (d)] in both the fcc and the hcp phases calculated at their respective equilibrium lattice constants.

much smaller than the corresponding effect on Hg. The differences between NR and SR DOS arise from the movement of the centers of l bands due to relativity and their subsequent hybridizations. The SR DOS also show that the centers of the d bands of Zn and Cd are deeper in the hcp phases than in the fcc phases. However, in Hg it is the fcc phase which has the lower d-band center than the hcp phase. The movement of the p-band center is consistent with the change in the s-p hybridizations; a lower (higher) p-band indicating increase (decrease) in the s-p hybridization.

We would like to point out that the electronic structure of Zn, Cd, and Hg described in this Letter, can be improved in a number of ways. Some of them are (i) use of no-shape approximation for the potential instead of spherically symmetric potential used in the ASA, (ii) the inclusion of spin-orbit terms, and (iii) the total energy optimization with respect to c/a and α for the hcp and the rhombohedral structures, respectively. These improvements can be quantitatively significant but the underlying physics governing the stability of different phases, namely the increase in s-p hybridization, is unlikely to change.

In conclusion, we have shown that the change in the most stable crystal structure from the hcp to the fcc-like rhombohedral structure in group II, as one goes from Zn to Hg is due to relativity. We have also shown that the increase in the s-p hybridization resulting from relativity is responsible for the stability of the scalar-relativistic fcc Hg over the hcp Hg.

This work was supported by the U.S. Department of Energy under Contract No. W-7405-Eng-48 with Lawrence Livermore National Laboratory.

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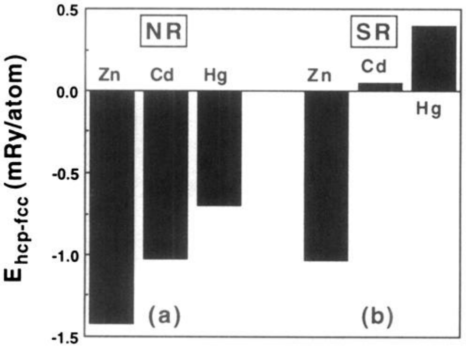

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