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1993 J. Phys.: Condens. Matter 5 8935

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The electric field gradient at the nucleus in HCP Zr and Hf

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Received 11 May 1993, in final form 27 August 1993

Abstract. We use the linear muffin-tin orbital formalism, in the atomic sphere approximation, to obtain the electric field gradient (EFG) at the nucleus for metallic Zr and Hf, in the HCP structure. Combined corrections are included in the calculations. To evaluate the importance of relativistic effects, non-relativistic and scalar relativistic calculations were performed. In agreement with experiment, we find that the EFG for Hf is larger than for Zr by a factor of more than 2. We show that this is mainly due to the behaviour of metallic p and d orbitals, which for Hf have comparatively larger values close to the nuclear region.

Because Hf and Zr are in the same group of the periodic table, Hf is often used as a probe in perturbed angular correlation experiments, when investigating the EFG for Zr alloys. We use our results to note that, for similar values of orbital occupations, the EFG at a Hf probe is larger than the EFG at a Zr atom placed at the same site.

1. Introduction

The electric field gradient (EFG) at the nucleus in solids can be measured by several techniques and a large number of experiments have been performed on metallic systems [1, 2]. Because of symmetry, the EFG is zero for monatomic metals with a cubic structure. Therefore, HCP metals are the simplest example of systems exhibiting non-trivial values of EFG. For a long time, simple point-charge models have been used to describe the lattice contribution for the EFG at a given site [3] and the Sternheimer factor has often been used to take into account the polarization of the electrons around the site. In 1988, Blaha *et al* [4] used the full-potential (FP) linear augmented-plane-wave (LAPW) method to obtain the EFG for a series of metals which form in the HCP structure. The series include 3d and 4d metals, but not Hf nor any other 5d transition-metal system. Their results, which agree extremely well with experiments, cast serious doubts on the validity of the empirical simplified models. It is clear from their results that the lattice contribution does not follow the well known Das-Pommerantz formula [1], based on the point-charge model, for HCP lattices. For example, Zr and Ru, both with a c/a ratio of about 1.59, show opposite signs for the lattice contribution when the FP LAPW formalism is applied. The FP LAPW results [4] also show that the core polarization is negligible in all cases and that the most relevant contribution comes from the valence electrons around the nucleus. The fact that reliable first-principles calculations are required in order to describe the EFG correctly is not surprising. It can be shown that [4, 5] the electronic contribution to the EFG depends on very small differences (of the order of 0.01 electrons) between the occupations of orbitals with different symmetries around the nucleus. It is clear that a good description of the electronic structure is needed in order to obtain this kind of accuracy. The linear muffin-tin orbital (LMTO) atomic-sphere-approximation (ASA) method [6] can be used to obtain values of the EFG for metals. This formalism, with the inclusion of combined corrections [7], has

been previously used with success to obtain the EFG for HCP Zr [8,9]. It can be shown that, within the LMTO ASA formalism, the EFG, to a good approximation, can be decomposed into a product of two terms [5]. One is due to small differences between the occupations associated with orbitals of distinct symmetries. To obtain this term, an accurate calculation of the band structure is required. The second term depends on the behaviour of the metallic p and d orbitals close to the nucleus and is not very sensitive to the environment around the atom. In this paper, by comparing the product of the two terms mentioned above with the values of the EFG obtained directly from the calculations for Zr and Hf, we numerically study this decomposition. This is done in a very general context, where the k -space LMTO ASA formalism including combined corrections and relativistic effects is used. Finally we use the decomposition into contributions from the occupation difference ΔN_p for p orbitals and the occupation difference ΔN_d for d orbitals and from the behaviour of the radial p function I_{pp} and radial d function I_{dd} close to the nucleus to understand the similarities and differences between the behaviours of the EFG for Zr and Hf. A better understanding of the problem may be of help to experimentalists when using Hf as a probe in the study of the EFG for Zr alloys.

In section 2 we give a brief description of the formalism and show how the electronic contribution to the EFG can be decomposed into two terms. The results and discussion are presented in section 3. Finally in section 4 we give the conclusions.

2. Formalism

The LMTO ASA formalism is well known and has been described in several papers [6,7]. In this section we give a brief introduction to the LMTO ASA formalism, mainly to point out the approximations used and to establish the notation. We also discuss in this section the two different approaches which were used to obtain the values of the EFG for Zr and Hf presented here.

The LMTO is a linear method and the solutions are most accurate near a freely chosen energy $E_{l,v}$. Here, as in most of the literature, $E_{l,v}$ is taken at the centre of gravity of the occupied part of the given ($l \equiv s, p$ or d) band. In our calculations we use the ASA, where the space is divided into Wigner–Seitz (WS) cells, which are then approximated by WS spheres of the same volume. When the ASA is used, the information needed to construct the Hamiltonian can be divided in two parts [6]. The first depends on only the structure (the position of the sites in space). The second depends on the solution of the Schrödinger equation at energy $E_{l,v}$, inside each inequivalent sphere, with appropriate boundary conditions. When solving the quantum-mechanical problem within the sphere, a relativistic approach can be introduced, if desired.

In this article we use the standard k -space LMTO ASA, with combined corrections included, to obtain the electronic structure and the EFGs for HCP Hf and Zr. Both non-relativistic (NR) and scalar relativistic (SR) calculations [10] were performed, yielding the corresponding charge density inside each WS sphere. By solving Poisson's equation for the total (electronic plus nuclear plus core) density, the electrostatic potential is calculated. The leading terms of the $l = 2$ components near the nucleus determine the EFG tensor V_{ij} , which must be diagonalized to obtain a value for the EFG. Details of the procedure can be found elsewhere [9]. For systems with axial symmetry (such as HCP) the tensor is diagonal and it is enough to consider the leading term of the ($l = 2, m = 0$) component of the electrostatic potential:

$$V_{zz} = A \lim_{r \rightarrow 0} \left(\frac{V_{20}(r)}{r^2} \right) = A \frac{8\pi}{5} \int Y_{20}(\hat{r}) \rho(r) \frac{1}{r^3} dr. \quad (1)$$

Here the integral is over all space excluding the nucleus, $\rho(r)$ is the charge density and $V_{20}(r)$ is the radial part of the $(l, m) = (2, 0)$ component of the electrostatic potential felt by the nucleus. The function $Y_{20}(\hat{r})$ is a spherical harmonic and A is a constant. This procedure was followed by Blaha *et al* [4] using the FP LAPW to generate the charge density. They have considered the group III and IV HCP metals and found that the valence contribution was clearly dominant. For the specific case of Zr it accounts for 93% of the effect. Hf was not included, but one should expect a similar behaviour. On the basis of these results, we consider only the valence contribution in our calculations.

Equation (1) is rather exact but not very transparent. It is not easy to predict the magnitude of the EFG, or the relative importance of p-p and d-d contributions. Physically it is clear that the number of electrons occupying orbitals with different symmetries is important. For example, in cubic systems, where the x , y and z directions are equivalent (yielding the same occupation) the EFG is zero. Blaha *et al* [4] have shown that the charge asymmetries ΔN_d and ΔN_p defined below are important to understand the behaviour of the EFG, but it is also clear that, if the charges are closer to the nucleus, they contribute more. Therefore, besides the occupation, the distribution of charges is important. If, for given occupations, the radial function is more significant close to the nucleus, the value of the EFG should be larger. It is interesting to obtain an expression for the EFG, which emphasizes these aspects. In a previous paper [8] we have shown that this can be done for the NR case. Here we generalize to include relativistic effects, within the SR approximation.

An alternative way to obtain an expression for the tensor V_{ij} associated with the EFG is to use the quantum-mechanical average of the classical EFG in the state Ψ_E , integrated in energy over the occupied state:

$$V_{ij} = 2 \int_0^{E_F} \langle \Psi_E | \frac{\partial^2 V}{\partial x_i \partial x_j} | \Psi_E \rangle dE. \tag{2}$$

In a LMTO ASA formalism, the wavefunction Ψ_E can be written in terms of radial solutions of the quantum-mechanical problem inside each WS sphere and its first energy derivative, both taken at energy E_ν . In the NR case these are solutions $\phi_{l,\nu}(r)$ (and corresponding energy derivatives $\dot{\phi}_{l,\nu}(r)$) of the Schrödinger equation inside the WS spheres, at E_ν . In the SR case, a similar expression for the wavefunction can be used, but the NR solutions $\phi_{l,\nu}(r)$ and $\dot{\phi}_{l,\nu}(r)$ have to be replaced by the Dirac bispinors $\Phi_{l,\nu}(r)$ and $\dot{\Phi}_{l,\nu}(r)$ (radial solutions of the SR equation inside the WS spheres). Following the procedure described by Koelling and Harmon [10], we find that in the SR expansion the radial solution of the Dirac equation inside the WS sphere takes the form

$$\Phi_{l,\nu}(r) = \begin{bmatrix} g_{l,\nu}(r) \\ h_{l,\nu}(r) + g_{l,\nu}(r) \frac{(K+1)}{2Mc r} \end{bmatrix}. \tag{3}$$

The upper and lower parts of $\Phi_{l,\nu}(r)$ are associated with the large and small components of the Dirac bispinor, respectively. Here c is the velocity of light, M the electronic mass and K is the spin-orbit coupling quantum number related to the angular momentum quantum number l in the usual manner [10]. We note that in the SR approximation, where the spin-orbit coupling is neglected, l and m are still good quantum numbers. In this case the SR wavefunction can be written in terms of $\Phi_{l,\nu}(r)$ and $\dot{\Phi}_{l,\nu}(r)$ in a very simple form, analogous to that of the NR case:

$$\Psi_E = \sum_{R,L} [\Phi_{Rl\nu}(r) + (E - E_\nu) \dot{\Phi}_{Rl\nu}(r)] Y_L(\hat{r}) u_{R,L}(E). \tag{4}$$

Here $Y_L(\hat{r})$ are the real version of the spherical harmonics and $u_{R,L}$ are the corresponding expansion coefficients, obtained by solving the eigenvalue problem, within the LMTO ASA formalism. The index L , related to (l, m) , determines the angular dependence of Ψ_E . To evaluate the EFG tensor using the SR approach, we substitute the above expression for the wavefunction Ψ_E in equation (2). As previously [8], we neglected the core contribution and contributions coming from charges located outside the WS sphere associated with the given nucleus. These contributions are usually small in metallic systems [4]. In this context when calculating $V_{i,j}$ in equation (2) at this site R , we can neglect all terms associated with sites R' different from R . By analogy to the NR approach, we have also neglected radial integrals involving $\hat{\Phi}_{l,\nu}(r)$. When this is done, the components of the tensor V_{ij} can again be expressed as a product of an energy-dependent integral (difference between occupations of orbitals with different symmetries) and radial integrals $I_{ll'}$. The expression for the component V_{ij} , given in [8], are still valid if we use for the radial integral $I_{ll'}$ a different expression involving the SR solutions. In the SR approach, the important integrals I_{pp} and I_{dd} , associated with p and d contributions to the EFG, are given by

$$I_{ll} = \int \left[\frac{|g_{l,\nu}(r)|^2}{r} \left(1 + \frac{l(l+1)}{2Mc^3r^2} \right) + \frac{|h_{l,\nu}(r)|^2}{r} \right] dr. \quad (5)$$

In this paper we are interested in HCP Zr and Hf. In these lattices, when the z axis is chosen along the c axis, the tensor V_{ij} is diagonal with V_{xx} equal to V_{yy} . The trace of the EFG tensor is always zero. Therefore, the EFG, defined as the largest component of the diagonal tensor in magnitude, is equal to V_{zz} in HCP lattices. As a consequence, the EFG in these lattices, for both SR and NR cases, can be written in terms of occupation differences and radial integrals in a very simple form:

$$V_{zz} = (e/\pi\epsilon_0) \left(\frac{1}{7} I_{dd} \Delta N_d + \frac{1}{5} I_{pp} \Delta N_p \right) \quad (6)$$

with

$$\Delta N_p = N_x - N_z$$

and

$$\Delta N_d = 2N_{xy} - N_{xz} - N_{3x^2-r^2}.$$

Here N_L is the occupation of the orbital with symmetry L , obtained from NR and SR LMTO ASA calculations. To obtain equation (6), we have used the HCP symmetry, for which

$$N_x = N_y$$

$$N_{x^2y^2} = N_{xy}$$

and

$$N_{xz} = N_{yz}.$$

In the SR case, the integrals I_{pp} and I_{dd} are defined by equation (5). In the NR case these integrals are simple averages of r^{-3} over the NR radial functions $\phi_{l,\nu}(r)$ [8]. The expression for the EFG for HCP lattices is rather transparent and will help in the analyses of our results on the EFG for Zr and Hf, which are obtained from LMTO ASA calculations, using NR and SR versions of the formalism.

3. Results and discussion

In this section we present our LMTO ASA results on the EFG for Zr and Hf. Combined corrections were included in the calculations. Initially, as in our previous work, NR codes were used, but Hf, being a 5d transition metal, is a heavy element, and relativistic effects may be important. Therefore, to evaluate the relevance of these effects to the EFG, we have also performed calculations using the SR approach. The results presented here were obtained using a minimum basis of s, p and d orbitals in the LMTO ASA formalism. We have also calculated the EFG including f electrons in the basis. For both Zr and Hf, the inclusion of f electrons changes the results by less than 1%. In table 1 we show our results on the EFG for HCP Zr and Hf, using the NR and the SR approaches. We see from table 1 that in both cases the SR corrections contribute to increase the value of the EFG and, as expected, they are larger for Hf than for Zr. For comparison, we also show in table 1 the experimental values of the EFG for Hf and Zr [2]. In the case of Hf there are several experiments by more than one technique [11] and their values shows a scatter of around 4%. Blaha *et al* [4] have obtained an EFG of 143×10^{13} esu cm⁻³ for Zr. As we have mentioned before, the EFG depends on very small differences between occupations of different symmetries and is extremely difficult to calculate. Considering the difficulties involved in the calculations, overall agreement between theory and experiment is rather good. We should note that the ASA approximation is the main limitation regarding the application of the method to HCP systems. It is known that, if combined corrections are not included, the EFG result for Zr is smaller by a factor of 2 [9]. We have verified that this is true in the case of Hf. Therefore, even though the NR results are closer to experiment than the SR data are, in the light of the present limitations, this better agreement is not significant.

Table 1. EFG for HCP Zr and Hf. Calculations were performed in the NR and SR approximations. The experimental values were taken from [2].

	EFG (10^{13} esu cm ⁻³)		
	Experimental	NR	SR
Zr	123	158	191
Hf	312	338	434

In this paper we would like to make a comparison between the behaviours of the EFGs for Hf and Zr. We note from table 1 that, even though the values vary, in all cases the ratio of the EFG for Hf to the EFG for Zr lies between 2 and 2.5. The same is true for NR and SR calculations when combined corrections are not included. Zr and Hf are very similar with respect to the behaviour of their valence electrons, and Hf has often been used as a probe to study the EFG for Zr compounds. It is therefore interesting to determine the origin of the factor of more than 2, found in both experiment and theoretical results on the EFGs for these metals.

In table 2, we show the values calculated for the charge asymmetries ΔN_l and the radial integrals I_{ll} associated with the orbital l ($l = p$ and d) within the WS sphere around the nucleus for Hf and Zr. The EFG, given by V_{zz} in equation 6, is defined as a function of these quantities. The value of the EFG obtained from equation 6, and its p and d contributions, are given for Zr and Hf in table 3. For comparison we also show the results obtained directly from the LMTO ASA calculations, using equation (1). From table 3 we see that the two different ways of obtaining the EFG give very similar results for both the NR

and the SR cases. (It is interesting to note that this is also true when combined corrections are not included.) Therefore we can use the values in table 2 to compare the behaviour of the EFGs for Hf and Zr.

Table 2. Charge asymmetries ΔN_l and radial integrals I_{ll} for the p and d contributions to the EFG for Zr and Hf. The calculations were performed in the NR and SR approximations.

	Zr		Hf	
	ΔN_l	I_{ll} (\AA^{-3})	ΔN_l	I_{ll} (\AA^{-3})
NR p	0.034	95.6	0.038	187.0
NR d	0.083	12.2	0.082	23.2
SR p	0.036	102.0	0.034	303.0
SR d	0.086	11.9	0.100	22.9

Table 3. The p, d and total contributions to the EFG for HCP Zr and Hf. Calculations were performed in the NR and SR approximations using equation (6) and equation (1); see text.

	EFG (Zr) (10^{13} esu cm^{-3})		EFG (Hf) (10^{13} esu cm^{-3})	
	Equation (6)	Equation (1)	Equation (6)	Equation (1)
NR, p	124.0	123.0	273.0	270.0
NR, d	27.8	35.4	52.0	68.0
NR, Total	151.0	158.0	325.0	338.0
SR, p	143.0	154.0	395.0	351.0
SR, d	28.2	37.1	69.0	83.0
SR, Total	171.0	191.0	458.0	434.0

According to equation 6 the EFG for HCP systems can be understood in terms of angular asymmetries and radial integrals for p and d orbitals. The radial integrals are always positive and, for a metallic system, these quantities are rather insensitive to the environment in which the probe is placed. Tables with values for these quantities can be found for several probes [9]. In contrast, the angular asymmetries ΔN_p and ΔN_d can be positive or negative and are extremely sensitive to the local environment. As a consequence, rather accurate band-structure calculations are required even to obtain the correct sign of the angular asymmetries. We can see from table 2 that the asymmetries ΔN_p and ΔN_d are very similar for Hf and Zr in both NR and SR cases, but the values of I_{pp} and I_{dd} are, in all cases, much larger for Hf than for Zr. Owing to the $1/r$ dependence of the integrand in I_{ll} , the behaviour of the orbital close to the nucleus is important for the radial integral. In this region the orbitals associated with the heavier Hf give a larger contribution. It is important to consider the metallic orbitals as solutions of the Schrödinger equation inside the given spheres. If the size of the WS sphere is not drastically changed, the behaviour of these functions close to the nucleus is not very sensitive to the local metallic environment in which the atom is placed, and the values for I_{pp} and I_{dd} given in table 2 can be used for a Zr or Hf probe in other metallic environments. The radial integrals should not be calculated from atomic functions. The p radial integrals obtained using atomic orbitals can be an order of magnitude smaller than those calculated using the metallic orbitals.

Our results for the EFG confirm the belief that Zr and Hf have similar band structures and charge asymmetries in the HCP structure, but the radial integral for Hf is larger than that for Zr, giving rise to the larger observed value of the EFG for this system. If the similarity of charge asymmetries also holds when Zr is substituted by Hf in a compound, the value of the EFG for Zr could be estimated from that for the Hf probe. This could be done by imposing that the ratio of the EFG at the Zr site in the compound to the EFG at the Hf probe should be approximately equal to the ratio of the EFG for Zr to the EFG for Hf in the pure metals. One simple example would be to evaluate the EFG for Hf in HCP Zr. From our analysis, we would expect it to be very close to that for pure Hf. The measured value is 288×10^{13} esu cm^{-3} , differing from that for pure Hf by less than 8%, as can be seen from table 1.

4. Conclusion

In this paper we have used the usual LMTO ASA formalism to obtain the EFG at the nucleus of Zr and Hf. We performed NR and SR calculations. We showed that the values of the EFG are increased when SR effects are included. In both cases the ratio of the EFG for Hf to that for Zr is a factor of more than 2. Our calculations showed that the band structures of the two materials are similar and the differences in occupations of the orbitals with different symmetries are nearly the same. The origin of the larger EFG for Hf was traced to the behaviour of the radial functions close to the nucleus. This behaviour is rather insensitive to the metallic environment in which the probe is placed. Therefore we suggest that a Hf probe may be used to study the EFGs for Zr compounds but, to infer the EFG for Zr, the results should be divided by a value of slightly more than 2.

Finally we note that the separation of the EFG into an angular asymmetry and a radial part can be done in general. Because the radial part does not vary much with the local environment (for a similar WS sphere radius), it can give *a priori* information about the magnitude of the effect. It can also predict whether dominance of the p contribution is to be expected.

Acknowledgments

We wish to thank Dr H Saitovich for a very useful discussion about the experimental aspects of this problem.

This work was partially supported by the Fundação de Amparo à Pesquisa do Estado de São Paulo and Conselho Nacional de Desenvolvimento Científico e Tecnológico.

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