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Validity regions of charge shift model

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Abstract. The charge shift model has been used to calculate electric field gradients (EFG) for various probe-host combinations. The comparison with the corresponding experimental values indicates that the validity of the model depends on sign and magnitude of the charge shift. The model agrees fairly well with experiments for the hosts having positive charge shift. The agreement is good for hosts having negative charge shift only if the magnitude is small (< 0·012).

Keywords. Charge shift model; alloys; electric field gradient.

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1. Introduction

The electric field gradients (EFG) in noncubic metals receive contributions from the positive ions and conduction electrons and may be written as

$$eq = eq_{\text{latt}}(1-\gamma_\infty) + eq_{\text{el}} \tag{1}$$

where $(1-\gamma_\infty)$ is the Sternheimer anti-shielding factor. The electronic part is difficult to calculate from a microscopic first principle analysis because the wave functions and crystal potentials are known for few systems only. However, the large amount of experimental data collected on pure metals and on dilute impurity alloys has revealed very interesting systematic trends of EFG. Raghavan *et al* (1976) pointed out that the electronic contribution of EFG is roughly three times as large as the ionic contributions and has an opposite sign. This trend known popularly as 'universal correlation' (UC) is very striking and no theoretical explanation based on first principle microscopic analysis is yet presented to explain it. Bodenstedt and Perscheid (1978) advanced the charge shift model which offered a simple method to estimate the EFG in *hcp* metals and explained the UC to some extent. The basic idea of the model is to assume that the conduction electrons may be replaced by spherical charge clouds in between the positive ions and their charges may be calculated by balancing the electrostatic and elastic stress. This model does not consider the local electronic contributions and, therefore, is expected to work for systems involving normal *s-p* metals. However investigations (Krusch and Forker 1980) on the EFG in transition metal systems indicate that in many cases the localised moment contributions are insignificant. One expects the charge shift model (CSM) prediction to be good for such transition metal systems. Verma and Rao (1981) have shown that EFG at ^{57}Fe in Zn, Cd and Ti are in good agreement with CSM. Maio *et al* (1982) have compared EFG at various probes in Ti and Re and obtained very good agreement for Re host. These comparisons have also shown

that for many cases the model remains valid even if the ionic radius of the probe is considerably larger than that of the host ion.

We have used CSM to calculate the EFG in almost all the systems with non rare earth *hcp* hosts where the EFG are experimentally known and the second order elastic constants are available. The calculated values are compared with experimental values and the conditions for validity of CSM are identified. Such comparisons are important for they lighten a possible mechanism which explains the so-called UC between ionic part and total EFG. Secondly, the comparisons for systems involving transition metals may indicate the relative contributions of localised electrons. The cases are classified according to their agreement with UC and CSM and broad inferences are drawn.

2. Calculation procedure

The details of the procedure of calculations are described by Bodenstedt and Perscheid (1978). The model is based on the assumption that the conduction electrons of the *hcp* metals may be replaced by spherical charge clouds situated midway between the positive ions. The charges on these clouds are obtained from the electrostatic stress developed and the resulting departure of the ratio c/a from ideal value $\sqrt{(8/3)}$. Pointwise summation over the lattice for the contributions from positive ions and negative charge clouds then yields total EFG.

The probe dependence of EFG is considered by assuming that the difference between effective ionic charges of probe and host changes the charges of the nearest neighbour negative clouds. Though it is only a rough approximation, it has successfully described the EFG in a number of systems. As the conduction electrons may have finite overlap with the ionic charges, there is an uncertainty in the effective values of charges on ions. We have made calculations for $Z_{\text{eff}}/Z = 0{\cdot}5, 0{\cdot}75$ and 1 which give a plausible range of predicted field gradients.

The lattice spacings are taken mostly from Pearson (1958), the elastic constants from Simmons and Wang (1971) and Sternheimer anti-shielding factors $(1-\gamma_\infty)$ from Feiock and Johnson (1969) and Sternheimer (1963).

3. Results and discussion

Calculations are made for five normal metal hosts and seven transition metal hosts with various probes (about 100 systems) and the results are summarised in table 1. The calculated EFG values in all the III B and IV B hosts have signs opposite to the experimental values. It seems that the assumption of CSM is not appropriate for these hosts and we exclude these systems from table 1. This point is discussed in § 3.1.

Some comparisons were also made earlier. Thus Verma and Rao (1981) have reported CSM calculations for Fe in Zn, Cd, Ti, Hf and Zr; Verma *et al* (1981) have compared their data on temperature variation of EFG in FeZr with CSM; Hermans *et al* (1981) have discussed CdZr and CdRe and Maio *et al* (1982) have reported their calculation on probes in Ti and Re. We include all such cases (about 19 cases) in our paper for completeness. The CSM values given in the table are those obtained with $Z_{\text{eff}}/Z = 0{\cdot}75$ for both host and probe. At these Z_{eff}/Z values, Bodenstedt and

Table 1. CSM calculations of EFG for non III B and non IV B metal hosts.

Probe $(1-\gamma_\infty)$	Host charge shift	Be (2) −0·1647 0·814	Mg (2) −0·0119 4·2	Zn (2) +0·1063 13·37	Cd (2) +0·1449 34·30	Tl (3) −0·0140 56·17	Ru (4) −0·0878 24·00	Re (7) −0·0118 51·11
Pure	Cal.	−0·35	−0·06	+2·99	+7·06		−6·95	−4·07
metal	Exp.	±0·05	±0·04	+3·42	+6·10	—	±0·49	−4·71
	K	1·83	3·45	2·59	2·49		1·50	2·39
B (3)	Cal.	−0·48	−0·01	+0·25				
0·8549	Exp.	±0·13	±0·11	±0·23	—	—	—	—
	K	3·15	31·85	2·67				
F (5)	Cal.	−0·57		+0·31				
0·7	Exp.	±2·17	—	−2·89	—	—	—	—
	K	44·92		24·68				
Fe (3)	Cal.	−5·71		+3·01	+2·75	−0·23	−2·50	−0·55
10·14	Exp.	−2·82	—	+2·65	+2·69	±1·74	−0·71	−0·50
	K	4·94		2·62	3·22	11·43	2·72	1·74
Ga (3)	Cal.			+3·23				
10·90	Exp.	—	—	±5·57	—	—	—	—
	K			4·18				
Ru (4)	Cal.	−16·61		+8·87	+8·05			
24·00	Exp.	±5·90	—	±3·80	±4·60	—	—	—
	K	4·48		1·98	2·61			
Cd (2)	Cal.	−14·87	−0·46	+7·68		−0·63		−1·65
34·30	Exp.	−0·80	−0·35	+6·59	—	±0·39	—	−1·45
	K	1·33	3·45	2·19		1·69		1·64
In (3)	Cal.			+7·71	+7·04			
26·00	Exp.	—	—	±12·12	+8·80	—	—	—
	K			3·90	3·84			
Sn (4)	Cal.				+7·82			
23·30	Exp.	—	—	—	±7·88	—	—	—
	K				3·83			
I (7)	Cal.			+10·49	+9·46			
17·84	Exp.	—	—	+24·93	±78·65	—	—	—
	K			9·69	37·94			
Hf (4)	Cal.	−47·75		+25·50			−19·98	
69·00	Exp.	−2·65	—	+3·23	—	—	±4·79	—
	K	1·54		1·29			2·71	
Ta (5)	Cal.	−50·92		+27·42			−20·61	−4·16
62·00	Exp.	±3·76	—	±12·30	—	—	−6·23	−5·51
	K	1·86		2·23			3·47	2·34
W (6)	Cal.			+28·69	+25·93			
55·70	Exp.	—	—	+7·97	±8·89	—	—	—
	K			1·89	2·34			
Ir (3)	Cal.	−24·20			+11·46		−10·61	−2·34
43·00	Exp.	±6·38	—	—	±8·60	—	±2·89	−3·55
	K	3·10			2·68		2·65	2·25
Rh (2)	Cal.	−10·69		+5·64	+5·14		−4·69	
19·00	Exp.	±4·82	—	±6·20	±4·80	—	±0·54	—
	K	4·59		3·03	3·12		1·70	

Table 1. (*Contd.*)

Probe $(1-\gamma_\infty)$	Host charge shift	Be (2) −0·1647 0·814	Mg (2) −0·0119 4·2	Zn (2) +0·1063 13·37	Cd (2) +0·1449 34·30	Tl (3) −0·0140 56·17	Ru (4) −0·0878 24·00	Re (7) −0·0118 51·11
Au (1)	Cal.	−20·08					−10·63	−2·76
66·00	Exp.	±2·16	—	—	—	—	±3·48	−2·99
	K	1·46					2·30	1·68
Hg (2)	Cal.	−26·53		+13·70	+12·59			−2·95
61·20	Exp.	−3·10	—	+13·50	+12·10	—	—	−3·09
	K	1·72		2·37	2·66			1·76
Os (4)	Cal.			+17·59	+15·97			−2·89
47·60	Exp.	—	—	±12·30	±5·82	—	—	−2·88
	K			2·61	2·02			1·91
Pb (4)	Cal.				+22·76	−1·55		
67·82	Exp.	—	—	—	±7·18	±0·82	—	—
	K				1·89	1·73		

The ionic charge Z used for different metals are given in parenthesis. Sternheimer anti-shielding factors are taken mostly from Feiock and Johnson (1969). All EFG are in units of 10^{17} V/cm^2.

Perscheid (1978) have observed agreement with experiments in zinc system. The range of EFG obtained by varying Z_{eff}/Z from 0·5 to 1 is typically $\pm 50\%$ around the values given in the tables. The experimental values of EFG are taken mostly from Vianden (1981) and are at room temperature. For some of the cases where room temperature data are not available, low temperature data are given. The correlation constant K given in the tables is $|(eq - eq_{\text{ion}})/eq_{\text{ion}}|$. For the cases where sign of eq is not measured, correlation constants are calculated with sign inferred from similar cases as discussed below.

3.1 *Sign of* EFG

The sign of CSM values of field gradient is opposite to that of ionic contribution for all the cases. This is expected as one of the main objects for proposing this model was to explain the UC. However, Ernst *et al* (1979) have pointed out that the EFG in systems with group III B and IV B hosts do not follow the general trend and the sign of total EFG and eq_{ion} are same. The so-far measured signs of EFG in the group III B and IV B hosts confirm this except for the cases of FeTi. The other cases where signs are known, are HfSc, AuY, CdTi, HfTi, HfHf, CdHf, TaHf, and HfZr, and in all these, eq_{ion} and eq have same sign. The CSM prediction of sign disagrees for all these cases. The only correct prediction of sign for group III B and IV B metals is for FeTi and here magnitude-wise also the model prediction is good. For the non-III B and non-IV B hosts the signs are predicted correctly for almost all the cases.

A study of the cases where signs of EFG are experimentally known (about 36 cases with *hcp* hosts) suggests that the signs of EFG are determined mainly by the host. In the systems considered here the few exceptions to this general behaviour are as follows. FeTi shows negative EFG but other probes in Ti show positive EFG, and ^{19}FZn shows negative EFG but other probes in zinc show positive EFG.

Assuming that the hosts are the determining factor for sign, we leave out the III B and IV B metal hosts for the further comparison and discuss the remaining cases with the assumption that eq and eq_{ion} have opposite signs.

3.2 *Normal and transition metals*

As the model does not consider the localised electronic contributions, the general feeling is that it may work only for normal probes. Table 2 classifies the cases into normal and transition probes. We see that the behaviour is mixed regarding normal and transition probes. Hf probe in all hosts show considerable deviation from CSM. Ru probe in different hosts also deviates from CSM. Results with Fe probe are by and large consistent with CSM.

Interesting results are obtained considering the cases hostwise. Zn and Cd hosts by and large obey the CSM predictions. For these two systems the charge shift δ is positive. Among other hosts, experiments with Mg host show consistency with CSM and that with Re show very good agreement. For both these systems the charge shift δ is negative but quite small compared to other systems. We have given the values of δ for $Z_{eff}/Z = 0{\cdot}75$. For Mg and Re these values are $-0{\cdot}0119$ and $-0{\cdot}0118$ respectively. Relatively large negative charge shifts are obtained for Be and Ru, $\delta = -0{\cdot}1647$ and $-0{\cdot}0878$ respectively and the CSM predictions of EFG for almost all probes in these hosts disagree with the measured values. The case of Tl is not very clear and more experimental data are needed to verify the above trend. We now try to explain the above observations with a plausible argument.

The total EFG at probe nucleus is obtained by summing over the lattice contributions from positive ions and negative charge clouds. It was shown by Bodenstedt and Perscheid (1978) that the contribution of the twelve nearest neighbour negative charge clouds is a good approximation to the total eq if c/a is greater than its ideal value $(8/3)^{1/2}$. The contributions from distant cells become important if $c/a < (8/3)^{1/2}$. The charge shift δ is positive when $c/a > (8/3)^{1/2}$ and is negative when $c/a < (8/3)^{1/2}$. In this model, the effect of a probe of different ionic charge on distant cells is neglected. Only

Table 2. Classification of systems in normal and transition probes.

	CSM consistent $0{\cdot}5 < X^+ < 1{\cdot}5$			Deviation from CSM indicated $1/3 < X < 0{\cdot}5, 1{\cdot}5 < X < 2{\cdot}5$			Strong deviation from CSM $X < 1/3, X > 2{\cdot}5$		
Normal probe	MgMg, BZn, CdCd*, HgCd*, CdTl,	CdMg*, CdZn*, InCd*, CdRe*, PbTl.	ZnZn*, HgZn*, SnCd, HgRe*,	GaZn,	InZn,	IZn*.	BeBe, CdBe*, FZn*,	BBe, HgBe*, ICd,	FBe, BMg, PbCd.
Transition probe	FeZn*, FeCd*, RhCd, TaRe*,	RhZn, RuCd, ReRe*, AuRe*,	OsZn, IrCd, FeRe*, OsRe*.	FeBe*, RuZn, OsCd,	RuBe, TaZn, IrRe*.	RhBe, WCd,	HfBe*, AuBe, FeTl, HfRu, RhRu,	TaBe, HfZn*, RuRu, TaRu*, AuRu.	IrBe, WZn*, FeRu*, IrRu,

+ X = experimental EFG/calculated EFG.
*signs of EFG measured.

Table 3. Classification of systems according to the applicability of universal correlation.

	CSM consistent				Deviation from CSM indicated			Strong deviation from CSM		
UC obeyed $2 < K < 5$	MgMg, FeZn*, OsZn, InCd*, HgCd*,	CdMg*, CdZn*, CdCd*, SnCd, TaRe*,	ZnZn*, RhZn, FeCd*, IrCd, ReRe*.	BZn, HgZn*, RuCd, RhCd,	FeBe*, GaZn, WCd,	RhBe, InZn, OsCd,	RuBe, TaZn, IrRe*,	BBe, HfRu, AuRu.	IrBe, TaRu*,	FeRu*, IrRu,
Deviation from UC indicated $5 < K < 6$ $1 < K < 2$	CdTl, AuRe*,	PbTl, HgRe*,	FeRe*, OsRe*.	CdRe*,		RuZn.		BeBe, TaBe, PbCd, RuRu,	CdBe*, AuBe, HfZn*, RhRu.	HfBe*, HgBe*, WZn*,
Strong deviation from UC $K > 6$ $K < 1$						IZn*.		FBe, ICd,	BMg, FeTl.	FZn*,

*signs of EFG are measured.

the charges of the nearest twelve clouds are altered. Hence the CSM predictions may be poor for different probe in a host with $c/a < (8/3)^{1/2}$ *i.e.* with negative charge shift. We find that the model works alright when $c/a < (8/3)^{1/2}$ provided the charge shift is small ($< 0{\cdot}012$) as in Mg and Re. When $c/a < (8/3)^{1/2}$ with large negative δ, even the EFG in pure metal is not correctly described by the model (Be, Ru). The hosts with $c/a > (8/3)^{1/2}$ are adequately described by CSM as expected.

3.3 *Universal correlation*

Maio *et al* (1982) have observed that whenever a system obeys UC the prediction of CSM is in good agreement with experiments. Such a result would be important, for it asserts that the factor responsible for deviation from both CSM and UC is the same and it is probably the localised electronic contributions. In the absence of such contributions, the normal electrons may have high densities in the middle of positive ions which may give rise to favourable agreement with both CSM and UC. From extensive calculations undertaken by us, classified in table 3, it seems that one should make a negative statement that "strong deviations from CSM predictions are observed, whenever a system does not obey UC". For the systems obeying UC, a majority are consistent with CSM but a significant number of systems violate CSM. Such systems are B and Ir in Be host, Pb, Os and W in Cd host, Fe, Hf, Ta and Ir in Ru host and Ta in Zn host. The deviations for Ru and Be hosts are expected on the grounds discussed in §3.2. For WCd, PbCd, OsCd and TaZn, perhaps the simplistic picture of probe-host coupling described in CSM is not adequate and local contributions are important.

4. Conclusion

Charge shift model is applied to a large number of probe-host combinations to calculate the EFG. The model predicts correct sign for cases with hosts not belonging to group III B or IV B of periodic table except for FZn. Magnitudewise the predictions of CSM do not agree with experiments if the UC is not obeyed. The cases where UC is obeyed, show mixed behaviour regarding CSM. Model values are in good agreement for Zn, Cd hosts where $c/a > (8/3)^{1/2}$. For hosts with $c/a < (8/3)^{1/2}$ the validity of the model depends on the magnitude of the charge shift δ. The CSM values of EFG are in good agreement with experiments for the host Re and Mg where the charge shift δ is small. For Ru and Be, where δ is large, the CSM values do not agree favourably with experiments.

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