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On the Polarity of Transition Metal Pyrites

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Earlier relations between the core electron binding energies and the effective charge have been tested for S, Fe, and Ni, by using the literature XPS data for FeS_2 and NiS_2. The effective charges on the metal atoms are +0.44 and +0.72, respectively. These values agree well with recently published *ab initio* calculations.

Transition metal dichalcogenides are of considerable importance to solid state physics. The energy level systems have been discussed in qualitative terms (*1, 2*). More quantitative calculations have also been attempted, e.g., by Kahn (*3*).

Recently, a detailed *ab initio* atomic-orbital based calculation by Bullett, appeared (*4, 5*), giving inter alia a quantitative description of the (s,p,d) population, e.g., the sulfur configuration of FeS_2 was found to be $s^{1.9}p^{4.4}$ and that for the iron atom was $s^{0.1}p^{0.1}d^{7.2}$. This result was explicitly stated in terms of polarity, $Fe^{+0.6}(S^{-0.3})_2$.

The purpose of this note is to apply to XPS data of pyrites the empirical relations between core level electron binding energies and the effective charge of the atom in question. These relations have been tested in our laboratory following an earlier suggestion by Siegbahn *et al.* (*6*).

Our original motivation for this study was to simplify the treatment of XPS data of solid state catalysts and other materials of possibly unknown structure. The plan in general terms is as follows:

For the elements of the early rows of the periodic table, *ab initio* methods are well established and provide rather consistent estimates of the effective charge of the atoms. For the heavier elements, however, there is still a considerable uncertainty in *ab initio* methods (*7*).

Striking examples of basis set effects are given, e.g., by Zeinstra and Nieuwpoort (*8*). Above all, the assignment of charges to the transition metal atoms in a molecule, is difficult because of the extremely diffuse character of the orbitals involved (*9*).

Therefore, we attempted to set up a series of *linear* relations between binding energies, E_b, for light elements and theoretically calculated charges. In general form

$$(E_b)_i = k_i q_i + (E_{b,0})_i \qquad (1)$$

Presently there exist such relations for C (*10*), N (*10*), O (*11*), F (*12*), Si (*13*), P (*14*), S (*15*), and Cl (*16*). For sulfur, e.g., Eq. (1) takes the form

$$E_b(S_{2p}) = 3.38\ q_S + 163.8\ \text{eV} \qquad (2)$$

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These relations are to be regarded as empirical and pragmatic tools.

Other relations between $E_{b,i}$ and q_i usually contain a term representing the molecular potential (Madelung and related effects). However, none of these empirical relations fulfills the strict demands of the theory (*17*). Therefore, we have adopted the form of Eq. (1) as it is the simplest.

One use of these tools which we have tested is the investigation of such metal coordination compounds, where the ligands of the complex, consist only of such atoms that are characterized by Eq. (1). If these relations operate well in the pragmatic sense, we can estimate the charges on the ligands from the XPS data (if well-calibrated, as shown below). As the total charge of the metal complex is known, one can thus calculate the effective charge of the central metal atom by difference.

In this way one is able to obtain for series of complexes a set of XPS data (E_b) and effective charges (q_M) for the metal in question. It is important to note, that no theoretical calculation on the transition metal complex was made to obtain the latter set.

A priori little is known about the analytical form of the relation—if any—between $E_b(M)$ and q_M. Not even the pragmatic success of the linear relation between the binding energies and the effective (calculated) charge of the light elements, Eq. (1), allows us to assume that there should exist a simple relation between the corresponding entities for the transition metal atoms.

Interestingly, it turned out (*18, 19*) that there were, indeed, some indications of very simple relations for the transition elements as well.

At present the following set of linear relations has been found (*18–21*):

$$E_b(\mathrm{Ni}_{2p\,\frac{3}{2}}) = 6.74q_{\mathrm{Ni}} + 848.3 \tag{3}$$

$$E_b(\mathrm{Pd}_{3d\,\frac{5}{2}}) = 4.45q_{\mathrm{Pd}} + 333.9 \tag{4}$$

$$E_b(\mathrm{Fe}_{2p\,\frac{3}{2}}) = 6.4q_{\mathrm{Fe}} + 704.1 \tag{5}$$

$$E_b(\mathrm{Cu}_{2p\,\frac{3}{2}}) = 1.5q_{\mathrm{Cu}} + 932.2 \tag{6}$$

In order to test these relations under as many different conditions as possible—for compounds differing in structures and polarities, as well as polarizabilities—we apply Eqs. (2), (3), and (5) to the XPS data on transition metal pyrites as reported recently by van der Heide and colleagues (*22*). In their careful study these authors present, inter alia, the core electron binding energies of FeS_2 and NiS_2 (Table I).

Before such a treatment can be applied, however, the calibration procedure of our XPS work (*23*) must be described. In order to avoid the uncertainty in the correction of E_b for the charging potential caused by irradiation on nonconducting samples, we in-

TABLE I

EXPERIMENTAL XPS DATA FOR FeS_2 AND NiS_2 (*22*) AND THE CORRESPONDING "EXPERIMENTAL" VALUES OF q_{Fe}, q_{Ni}, AND q_{S}

	E_b (eV)							
Compound	$\mathrm{Fe}_{2p\,3/2}$	$\mathrm{Ni}_{2p\,3/2}$	$\mathrm{S}_{2p\,3/2}$	"S_{2p}"[a]	q_{Fe}	q_{Ni}	q_{S}	a (eV)
FeS_2	706.7		162.4	162.8	+0.44		−0.22	−0.2
NiS_2		853.6	162.7	163.1		+0.72	−0.36	+0.4

[a] In the experiments originally establishing Eq. (2) (*15*), we did not achieve the high resolution which has been attained in the present work (*22*). In order to conform to Eq. (2) the E_b values of van der Heide *et al.* (*22*) have been increased by 0.4 eV, representing the position of the composite peak maximum (which we used (*15*)) relative to that of the $S_{2p\,\frac{3}{2}}$ component (*24*).

troduced the use of an internal standard, namely the phenyl group.

The mean C_{1s} binding energy of the five unsubstituted carbons was used as a point of reference. In order to compensate for any chemical differences encountered by this phenyl group a secondary calibration using ir intensity data of the C–H stretching was developed (*23*). It is by use of this method that we have been able to establish Eq. (1) and thereby avoided the uncertainty in data that so often prevents an intercomparison of XPS data from different laboratories.

It may be possible that use of this internal standard decreases the difference between the readings of binding energies of the very surface atoms and those of the bulk material.

Thus it becomes obvious we cannot apply Eqs. (2), (3), and (5) directly to the data of van der Heide *et al.* (*22*), as their specimen did not contain an internal standard, i.e., a phenyl group. However, if one assumes that the difference in calibration remains the same throughout the entire spectral range, one can write for any atom i of the molecule,

$$E_{\mathrm{b},i} = a + E'_{\mathrm{b},i}, \tag{7}$$

where $E_{\mathrm{b},i}$ is the experimentally measured binding energy and $E'_{\mathrm{b},i}$ is the binding energy which would have been found, had it been possible to apply our method of calibration.

It is therefore $E'_{\mathrm{b},i}$ which should satisfy Eqs. (2), (3), and (5); hence we can write

$$E_{\mathrm{B},i} = a + k_i q_i + (E_{\mathrm{b},0})_i, \tag{8}$$

where k_i and $(E_{\mathrm{b},0})_i$ are the parameters of Eq. (1). For the solid samples one can expect a to be of the order of ±1 eV.

Results and Discussion

We now have all the necessary data. From the data in Table I we can formulate the following set of equations:

$$\begin{aligned} 162.8 &= a + 3.38q_{\mathrm{S}} + 163.8 \\ 706.7 &= a + 6.4q_{\mathrm{Fe}} + 704.1 \\ 0 &= 2\,q_{\mathrm{S}} + q_{\mathrm{Fe}} \end{aligned} \tag{9}$$

The last of these equations expresses the assumption that the crystal of FeS_2 is electrically neutral. This means that there is no charge transfer to or from the sample support and that the calibration is made against substances for which charging effects due to irradiation are negligible (*23*).

The values that emerge from the solution of Eqs. (9) are given in Table I, as are the corresponding ones for NiS_2.

One observes striking agreement between our "experimental" q_{M} values and those reported by Bullett (*4*, *5*) from *ab initio* calculations. The close agreement is emphasized by a graphical display (Fig. 1). Bearing in mind that Bullett reports his data to only one decimal place, the agreement is good, also with respect to the trend within the periodic system.

This close agreement seems to indicate three points:

First, the method of calculation used by Bullett conforms with those applied to the

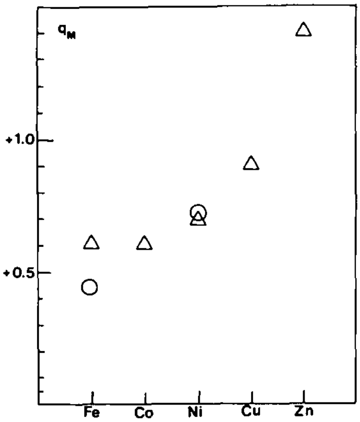

FIG. 1. The effective charge, q_{M}, of the metal atom in MS_2. △, Results of Bullett (*4*, *5*). ○, Results of the application of Eqs. (2), (3), and (5) of the present paper.

compounds of upper row elements which were utilized in papers (*10–16*).

Second, the linear relations of type Eq. (1) seem to be applicable also to iron and nickel.

Third, the assumption of a rather small a, constant over the whole spectral range, is justified.

Of course, the three propositions above may later turn out to be incorrect. More will be learned as additional systems are studied.

In closing it might be important to point out that this "experimental" determination of q_{Fe}, q_{Ni}, and q_S rests on quantum chemical calculations (from a large range of sources) on very simply, small molecules or ions, such as NO_3^-, SO_4^{2-}, SCN^-, chlorobenzene, etc, which were used to establish the relations (1) for the light elements. The analysis of the transition metal systems could be improved as better calculations become available.

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