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ELECTRON CAPTURE IN METAL (II) HALIDES

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ABSTRACT

The observation by Mossbauer emission spectroscopy of anomalous charge states of ^{57}Fe after electronic capture in ^{57}Co labeled metal (II) fluorides can be explained in a thermodynamic model when assuming that the preceding nuclear process involves after 10^{-7} sec only a constant excitation energy, stored in the immediate environment of the decayed nucleus. The experimental evidence of the existence of a threshold energy for stabilization of anomalous ionic species is justified by the theory, which agrees also with the nature and the increase of the proportion of anomalous charge species. The calculations take into account the variation of electrostatic energy and the size effect associated with the replacement of Fe^{+n} by $\text{Fe}^{+n'}$ in a substitution site of the lattice. The condition for stabilization of oxidized ionic species implies that this variation of energy must be higher than the threshold energy.

INTRODUCTION

A number of recent experimental works reported the observation by Mossbauer spectroscopy of anomalous charge states of ^{57}Fe after electronic capture of ^{57}Co in various host lattices¹. Electron capture is followed by an Auger

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cascade, which gives rise to highly charged ions. Time delayed coincidence measurements ² showed that the species observed by their Mossbauer emission spectrum are stable on a time scale from 5×10^{-9} to 3×10^{-7} sec after the nuclear event. Whereas the stabilization of anomalous charge states could be explained in several compounds with complex ligands, labeled with ⁵⁷Co, on the basis of a local autoradiolysis of the ligands by the X rays and electrons emitted during the Auger cascade, ^{3, 4} no satisfactory explanation could be found in the case of compounds with simple ligands.

A recent study of the nature of the iron after ⁵⁷Co EC in a series of metal (II) fluorides ⁵, provided opportunity to propose a thermodynamical model for these results. The normal charge state of iron in all these compounds is divalent, as proved by the absorber experiments of the corresponding ⁵⁷Fe labeled salts. The discontinuity of the proportion of Fe⁺³ along the series of salts (Table I) suggests that a minimal energy has to be transferred to the iron ions in order to stabilize the higher oxidation state. The model here developed justifies this observation.

CALCULATIONS AND RESULTS

It may be supposed that the neutralization of the highly charged species (Feⁿ⁺, $n \leq 7$) formed during the Auger cascade (10^{-15} sec) proceeds in the solid phase much faster than 10^{-7} sec, which is the mean life time of the first nuclear excited level of ⁵⁷Fe. After a time of 10^{-7} sec, the influence of the preceding nuclear process can be described as due only to some stored lattice excitation energy in the immediate vicinity of the nuclear disintegration site. A part of it (Exc) can be transferred to the iron ion. This excitation energy is expected to be nearly constant in a series of isostructural compounds, because of the similarity of the environment of the iron ions. As a consequence, the threshold energy for stabilization of

anomalously charged species is (IP-Exc), where IP is the ionization potential, in the solid phase, of the normal charge state.

The value of the threshold energy (IP-Exc) can be determined from an evaluation of the variation of potential energy associated with the substitution of Fe^{+2} by Fe^{+3} in a series of compounds with similar structure and a comparison with the proportion of the anomalous charge state as deduced from the Mossbauer emission spectra.

The first order term of this variation of energy is evaluated by calculating the electrostatic potential at a nucleus site in a crystal lattice, and considering then the effect of the variation of charge when replacing Fe^{+2} by Fe^{+3} . In agreement with the low value of the recoil energies associated with the electronic capture and Auger cascade processes ($E_R \leq 3.4$ eV) it has been shown that the iron ions stay at a substitution site in the crystal lattice⁶. The computation of the potential is done using a point charge model, with Ewald's method for calculating Madelung constants.

The electrostatic potential at the site of the nucleus i is $V_i = \sum_{j=1}^{\infty} \frac{e_j}{r_{ij}}$ where e_j are the point charges in the lattice, and r_{ij} their distances from the site under consideration. The electrostatic energy of an iron ion is $U(\text{ES}) = e_i e_{j1} \bar{\psi} + \sum_{j=1,5} e_i e_j \psi_{ij}$ where e_i is the charge of the iron ion, e_{j1} the charge of the host lattice cations, $\bar{\psi}$ the "ground potential" of a primitive lattice with unit charges, ψ_{ij} the potential created by such a lattice at the site of e_i . $\bar{\psi}$ and ψ_{ij} have been evaluated using Ewald's method, which transforms the slowly convergent summations into a calculable form⁷. They are then written:

$$\bar{\psi} = -\frac{1}{\sqrt{\pi\eta}} - \frac{4\pi\eta}{V_z} + \sum_{\eta \neq 0} \frac{1}{A\eta} G\left(\frac{A\eta}{2\sqrt{\pi}}\right) + \frac{4\pi}{V_z} \sum_{m \neq 0} \frac{e^{-(2\pi Bm)^2 \eta}}{(2\pi Bm)^2}$$

$$\psi_{ij} = \sum_{n=0}^{\infty} \frac{1}{|R_j - An|} G\left(\frac{R_j - An}{2\sqrt{\eta}}\right) - \frac{4\pi\eta}{V_z} + \frac{4\pi}{V_z} \sum_{n \neq 0}^{\infty} \frac{e^{-(2\pi Bm)^2 \eta + i2\pi Bm R_j}}{(2\pi Bm)^2}$$

The signification of the various terms is the following: the position of the ions in the rutile type unit cell are defined by the coordinates $(R_j): (a, a, b)$ and $(\frac{a}{2}, \frac{a}{2}, \frac{b}{2})$ for the cations, $(c, c, 0)$, $(a-c, a-c, 0)$, $(\frac{a}{2} + d, \frac{a}{2} - d, \frac{b}{2})$ and $(\frac{a}{2} - d, \frac{a}{2} + d, \frac{b}{2})$ for the anions.

V_z is the unit cell volume $(\vec{a} \times \vec{a}) \cdot \vec{b}$.

A is the vector (a, a, b) and An the vector $(n_1 a, n_2 a, n_3 b)$ where n_1, n_2, n_3 are the indices of the origins of the successive cells. The corresponding vectors in the reciprocal space are respectively B and Bm .

$G(x)$ is defined as $G(x) = 1 - \text{erf}(x)$ where $\text{erf}(x)$ represents the Gaussian error function $\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx$.

η is an arbitrary constant, which is introduced when arranging $\bar{\psi}$ and ψ_{ij} in a summable form; the numerical calculations have been checked by using two different values for η .

This method enables us to calculate the electrostatic energy of an iron ion situated in a host matrix as a function of the point charge values and the lattice parameters ⁸.

An important correction to the preceding calculations has been introduced by taking into account the size effect. Let us suppose that the introduction of a smaller ion (Fe^{+3}) than the host matrix cations does not perturb the lattice arrangement, and so does not modify the calculations. The introduction of a larger ion (Fe^{+2} in ZnF_2 , CoF_2 , NiF_2 and MgF_2) implies a compression, which can be supposed in a simple approximation to act only on the first coordination shell. This additional energy stabilizes further the ferric ions.

against the ferrous ones in these lattices by a quantity expressed as:

$$6 e_i e_j \left(\frac{1}{\sum r_{ion}(M^{++} + F^-)} - \frac{1}{\sum r_{ion}(Fe^{++} + F^-)} \right)$$

where we consider that the interionic equilibrium distances are the sums of the ionic radii.

The lattice parameters for the metal II fluorides are known with a good precision from the work by Baur⁹; we used in the calculations the experimental a, b, c, d values, as given in Table I.

The point charges were attributed + 2e for the metal cations and -e for the fluorine anions in all the compounds. These values are justified by the highly ionic bonding in these compounds. The main point is that the ionicity is constant along the series as is concluded from the nearly constant isomer shift of the iron species. On the other hand, it is well known that the point charge model works best for computing lattice energies when using the formal charge numbers and the experimental distances because of the self compensating features of this approximation¹⁰.

The variation of charge (Δch) on substituting Fe^{+2} by Fe^{+3} is a constant, and a reasonable values for (Δch) may be taken as $\Delta ch = 0.3e$ ¹¹. The last column of the table reports the calculated values for the variation of potential energy on substituting Fe^{+2} by Fe^{+3} with this figure for Δch , so as to give an idea of the numerical values along the series of compounds.

Compound	r_{ion} Å	%Fe ⁺³	Lattice Parameters (Å)			$\Delta U(ES)/\Delta ch$ eV	$\Delta U(Comp)$ eV	ΔU ($\Delta ch = 0.3$) eV
			a	b	$\frac{c}{a} = \frac{d}{a}$			
MnF ₂	0.80	00	4.8734	3.3099	0.305	20.77		6.23
FeF ₂	0.74	00	4.6966	3.3091	0.300	21.24		6.38
ZnF ₂	0.73	01	4.7034	3.1335	0.303	21.50	0.42	6.87
CoF ₂	0.72	32	4.6951	3.1796	0.306	21.50	0.84	7.29
NiF ₂	0.69	59	4.6506	3.0836	0.302	21.85	2.1	8.65
MgF ₂	0.66	82	4.623	3.052	0.303	22.30	3.5	10.20
Fe ²⁺	0.74							
Fe ⁺³	0.64							

Table I: Cation ionic radius (r_{ion}), percentage of Fe⁺³ in the emission spectrum⁵ lattice parameters⁹, variation of electrostatic energy $\Delta U(ES)$, variation of compression energy $\Delta U(comp)$ and typical value for ΔU with $\Delta ch = 0.3$, in the series of metal II fluorides.

DISCUSSION

The series of calculated ΔU shows a monotonical increase in the same order as the percentage of Fe⁺³ formed in these salts after⁵⁷ Co EC. The threshold energy required for stabilization of Fe⁺³ in these compounds is thus (IP-Exc) ~ 6.87 eV, i.e. the value of ΔU in the compound where Fe⁺³ begins to appear.

For the three compounds CoF₂, NiF₂ and MgF₂, the increase of the ratio of the percentages of Fe⁺³ and Fe²⁺: $K = \frac{Fe^{3+}}{Fe^{2+}}$ follows a logarithmic proportionality law: $\log K \propto [\Delta U - (IP-Exc)]$. Supposing that the law of mass action applies to the present phenomenon, it can be deduced that the local temperature

would be of the order of magnitude of 14000°K . Such a high temperature could agree with the concept of a localized intense lattice excitation, or a thermal spike following the nuclear process in the solid state.

The relation $\Delta U > IP - \text{Exc}$ should be a sufficient condition for the observation of anomalous oxidized species in compounds with similar structure, where the defects created by the autoradiolysis remain identical. There may be some difficulties when comparing the results obtained in very different host lattices because the defects and the excitation energy (Exc) may vary considerably. On the other hand, the calculation of ΔU can be rather laborious, depending on the crystal structure. $\Delta U(\text{ES})$ may however be shown to increase with the Madelung constant, or the lattice energy of the host matrix. When the size effect does not exist, which is the case in all Co^{+2} compounds for example, it is thus expected that the proportion of the oxidized species increases with the Madelung constant of the lattice. Such an empirical correlation has already been mentioned.¹²

The model allows an explanation for a number of experimental facts. Because of a high increase in the values of the successive ionization potentials, it is expected that only one additional charge number against the normal ionization state should be stabilized. This is in accordance with the experimental data, obtained in all the simple ligand compounds except the case of the ^{57}Co doped metal oxides, where additional charge states of ^{57}Fe were observed. Uncertainties are however introduced in the study of the oxides because of the difficulty of using stoichiometric compounds. The importance of diffused impurities is revealed by the discrepancies between different authors' results obtained in ^{57}Co doped oxides¹³. Similarly, in the case of ^{57}Co : AgCl , Fe^{+3} only appears after annealing in air¹⁴.

In anhydrous cobalt (II) chloride, iron is only observed in the divalent state ¹². Because of the low value of the Madelung constant of its structure (type CdCl₂), it can be deduced that ΔU will be low, which means that in CoCl₂, $\Delta U(\text{ES})$ must be smaller than (IP-Exc). On the other hand K₃CoF₆ is one of the few compounds where the presence of Fe⁺⁴ was observed. This compound has also a very high value of the Madelung constant (cryolite type structure), such that $\Delta U(\text{ES})$ must be higher than (IP¹-Exc), where IP¹ is the ionization potential of Fe⁺³ ¹⁵.

Considering now the case of the ⁵⁷Co doped monovalent halides, we assume that the "normal" charge state for iron impurities is +1. In silver chloride, the variation of electrostatic energy when substituting Fe⁺² for Fe⁺¹ and Fe⁺³ for Fe⁺² is $\Delta U(\text{ES}) = 4.5 (\Delta\text{ch}) \text{ eV}$. $\Delta U(\text{ES})$ is high enough to stabilize Fe⁺² in this lattice; comparing however this value with $\Delta U(\text{ES})$ calculated in the metal (II) fluorides, the former is seen to be much lower; it is thus predicted that that in ⁵⁷Co: AgCl only divalent iron will be formed, in agreement with the experimental data. A similar explanation applies to the cases of NaF and NaCl ¹⁶. Among these three compounds, $\Delta U(\text{ES})$ is lowest in NaCl, which justifies a possible observation of Fe⁺¹ in this salt.

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