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Abstract

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ON THE EVALUATION OF THE CHEMICAL BOND FROM THE HYPERFINE STRUCTURE OF THE ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF MANGANESE

(Presented by Academician N. V. Belov, 25 XI 1963)

A decrease in the magnitude of the splitting A of the hyperfine structure (h.f.s.) of the electron paramagnetic resonance (e.p.r.) spectra of impurity ions Mn^{2+} on going from fluorides and oxides to sulfides, selenides, tellurides, i.e., from more ionic to more covalent compounds, was noted by Van Wieringen (^{1}) and considered for octahedral complexes $M—X_6$ within the framework of Owen' s molecular-orbital method (^{2}) in 1955. At present, the influence of bond covalency on the h.f.s. of e.p.r. spectra is shown mainly on the basis of these data ($^{3-5}$). The h.f.s. values measured by us for 28 minerals and the published measurements, which together constitute data for almost 80 compounds (instead of the 12 available to Van Wieringen), make it possible to draw certain conclusions about the use of the h.f.s. for evaluating the state of bonding in minerals and inorganic compounds.

Table 1

Hyperfine-structure constant A, in 10^{-4} cm^{-1}, in binary compounds (1, 3, 4, 6, 7)

	F	Cl	Br	O	S	Se	Te
K	–	88.6	88.6	–	–	–	–
Na	91.5*	82.1*	–	–	–	–	–
Li	–	76.0	–	–	–	–	–
Ag	–	81.0	77.0	–	–	–	–
Mg	90.6*	82.0	–	81.6	71.9	71.2	58.1
Ca	94.8**	–	–	84.5**	75.7	72.9	67.2
Sr	93.0	87.0	–	–	75.2*	–	–
Ba	91.0	–	–	–	–	–	–

	F	Cl	Br	O	S	Se	Te
Cd	91.8*	82.0	–	–	63.6	61.5*	57.0*
Zn	92.0	–	–	77.0*	64.0 63.8	60.0	56.0
Al	–	–	–	79.2*	–	–	–

* Mean value from 2-3 determinations differing by no more than $1 \div 2 \cdot 10^{-4}$ cm^{-1}.
** Mean of 3 determinations differing by $4 \div 5 \cdot 10^{-4}$ cm^{-1}.
The regions of the structural types NaCl–MgO (6:6), CaF_2 (8:4), TiO_2–MgF_2, ZnF_2 (6:3), $CdCl_2$ (6:3, layered), ZnS (4:4), Al_2O_3 (corundum) are indicated.

Table 1 gives data for binary compounds, and Table 2 for certain other inorganic compounds. Table 3 gives data on minerals. Measurements were carried out on single crystals of natural minerals containing $0.0n$—$0.00n$% Mn^{2+}, at room temperature, on an RE-1301 (EPR-2) radiospectrometer at a frequency of 9300 MHz. The resonance positions of the magnetic field were determined by superposing, on an oscilloscope, the maxima of the derivative absorption signal with the signals of a proton sensor (IMI-2).

The electronic configuration of Mn^{2+} is $3s^2 3p^6 3d^5$, ${}^6S_{5/2}$, but it is necessary to take into account (^{14}) the admixture of the excited configuration $3s3p^6 3d^5 4s\ {}^6S$. According to quantum-mechanical theory, it is specifically for s-electrons that there is a definite probability of being at small distances from the nucleus. This also provides the possibility of interaction of the unpaired $3s$-electron with the nucleus Mn^{55} (nuclear spin 5/2), manifested in the form of an isotropic contact h.f.s. The h.f.s. constant A is related to the effective nuclear charge $z^* = z - \sigma$ (σ is the shielding constant) and the effective principal quantum number $n^* = n - \Delta$ (Δ is the quantum defect) by the relation

$$A = \frac{8}{3} \mathrm{R} \alpha^2 g(I) \frac{z^{*3}}{n^{*3}},$$

where R is the Rydberg constant, α is the fine-structure constant, and $g(I)$ is the g-factor of the nucleus. Physically, the effect of bond covalency on the h.f.s. can be represented as a decrease in the interaction of the $3s$-electron with the nucleus as its interaction with the surrounding ions increases, drawing away the paramagnetic electron and shielding it from the nucleus.

Various experimental quantities sensitive to changes in the chemical bond (h.f.s. in EPR, the chemical shift in nuclear magnetic resonance, quadrupole interaction, electron densities from Fourier syntheses, x-ray absorption spectra, dielectric permittivity, etc.) reflect the total effect of various, although interrelated, physical phenomena accompanying changes in the state of the chemical bond. At the same time, only a definite aspect of this complex phenomenon is reflected. This is what accounts at present for the approximate, evaluative approach to describing the state of a bond. Usually it is possible to establish the sequence of compounds in a series obtained from one of these constants, while the absolute values characterizing the ionicity-covalency of the bond are much less convincing.

Table 2

H.f.s. constant $A \times 10^{-4}$ cm^{-1} in some inorganic compounds (3, 4, 6, 8, 9)

Compound	$A \times 10^{-4}$ cm^{-1}	Compound	$A \times 10^{-4}$ cm^{-1}
$(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$	92.5	$BaTiO_3$	81.6
$(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$	91.0	CaTl	67.2
$MgSO_4 \cdot 7H_2O$	88.0	CdTl	58.1
$Mg_3Bi_2(NO_3)_{12} \cdot 24H_2O$	90.0	ZnTl	56.0
$MgSiF_6 \cdot 6H_2O$	92.3	GaAs	52.6
$KMgF_3$	91.8	Si	53.5
$CsCaF_3$	90.8	Ge	42.5

Let us first consider changes in the h.f.s. A in simple compounds (Table 1 and partly Table 2, Fig. 1) with one and the same cation but different anions, for example in the compounds MgF_2, $MgCl_2$, MgO, MgS, MgSe, MgTe. The presence in this series, and in series with other cations, of compounds belonging to one structural type (see Table 1) makes it possible to establish more reliably the following sequence of decreasing h.f.s. (which is associated with decreasing ionicity): F—Cl—O—S—Se—Te.

Fig. 1. Change in the magnitude of the hyperfine-structure splitting A h.f.s. in binary compounds (from the data of Table 1)

Consideration of the vertical series in Fig. 1 leads to the following conclusion: in compounds with one and the same anion, very considerable variations of A h.f.s. are observed as a function of the cation replacing manganese. Thus, in oxides A h.f.s. varies from values observed in sulfides ($A\mathrm{ZnO:Mn} \simeq A\mathrm{CaS:Mn}$) to values almost equal to the A h.f.s. of fluorides (see Table 3). This means that the ionicity of the Mn—O bond changes from that characteristic of some sulfides ($\sim$ 50-60% ionicity, see below) to that characteristic of fluorides ($\sim$ 90% ionicity). Similar variations of A h.f.s. within $13 \div 15 \cdot 10^{-4}$ cm^{-1} are also observed in chlorides, sulfides, selenides, and tellurides. Only in fluorides does A h.f.s. vary within very narrow limits (from 91 to $95 \cdot 10^{-4}$ cm^{-1}). At the same time, A h.f.s. decreases in the same sequence in all the groups of compounds studied: Ca—Sr—Mg—Cd—Zr. Obviously, if more ionic and more covalent compounds are studied within each group, the variations of A h.f.s. will correspondingly increase. Thus, A h.f.s. of Mn^{2+} reflects the state of the Mn—X bond

Figure 2

Figure 1: Figure 2

in a given compound KX with a definite structure and with the cation K replaced by manganese. A special feature of estimating the bonding state from the h.f.s. of Mn^{2+} is that Mn^{2+} is present as an impurity. This feature is closely connected with the specifics of the EPR method.

The presence of paramagnetic ions as an impurity with a content of 1 : 1000 or less leads to the fact that the state of the Mn–X bond is, to a very large extent, subordinated to the state of the K–X bond. In order to satisfy the condition of conservation of the balance of effective charges, the effective charge of manganese must be determined almost entirely by the effective charges of the cation that accommodates the impurity ion of the compound (not taking charge compensation into account). For example, in a structure of the MgO(NaCl) type, with a content of 0.1% Mn per 1000 Mg–O_6 octahedra there is one Mn –O_6 octahedron. Each oxygen of the Mn octahedron simultaneously belongs to five Mg octahedra. In each Mg octahedron, the effective charges of the five oxygens shared with other Mg octahedra remain characteristic of the Mg–O bond in the given compound. Thus, the effective charge of each oxygen of the Mn octahedron is already determined in a ratio of 25 : 1 by the state of the Mg –O bond, which forces the state of the Mn–O bond also to adapt. This rough scheme agrees with the above-noted changes in the Mn–X bond in different KX compounds.

Fig. 2. Approximate dependence between A of the h.f.s. and the degree of ionicity. 1–according to Matumura (6), 2–according to Van Vyringen (1), 3–proposed curve

Thus, the h.f.s. of Mn^{2+} has a more general significance: it characterizes the state of the K–X bond, where K is the atom replaced by manganese. From this point of view, all ions present as an impurity in some compound must have effective charges identical and close to the effective charge of the substituting ion. Determination of the effective charges of impurity ions from the h.f.s. in one and the same compound (for example, Mn^{2+} and V^{2+} in MgO) would be a test of this conclusion. These observations, as well as EPR data such as the incorporation of the large Gd^{3+} ion into the corundum lattice (15) Al_2O_3, show that impurity ions in compounds are in a special state.

Let us try to estimate the bonding states semiquantitatively from the h.f.s. First we shall consider the limiting states.

a) The most ionic are the fluorides–NaF, CaF_2, etc. In them the maximum h.f.s. splittings are observed (A up to $92 \div 95 \cdot 10^{-4}$ cm^{-1}). This is the upper limit of A of the h.f.s. of Mn^{2+} in crystalline substances, corresponding to the most ionic state. However, observations of the "superhyperfine" structure in fluorides (16), due to the interaction of the unpaired electron of Mn^{2+} with the F^{19} nuclei, indicate the presence here of a certain covalency of the bond. This means that there are no minerals or inorganic compounds with a purely ionic bond.

b) The most covalent and purely covalent among the investigated compounds are the semiconductor compounds GaAs, Si, Ge. To a considerable extent the properties of Mn^{2+} are leveled out because of its presence as an impurity; moreover, the Mn–As, Mn–Si, Mn–Ge bonds are apparently closer to purely covalent than the Mn–F bond is to purely ionic.

To estimate intermediate states we shall use data on effective charges determined from the dielectric constant (17), see the discussion in (18).

On the basis of all these data, Fig. 2 shows an approximate dependence between the degree of ionicity of the bond and A of the h.f.s. For comparison, there are given

straight lines according to Van Wieringen (1), who proceeded from an arbitrary assumption of a rectilinear dependence between A and the degree of ionicity and extrapolated the covalent values of the h.f.s. to zero, and according to Matumura (6), who used Pauling electronegativities referred to valence to estimate the state of the bond. These straight lines give a sharp overestimate of the ionicity of the bond (the Mn^{2+} bond in Si is obtained from them as 50 and 75% ionic).

Minerals for which h.f.s. data are available (Table 3) belong to oxygen salts (except sphalerite); in them Mn^{2+} replaces non-radical–

Table 3

Constant A of the h.f.s. ($\times 10^{-4}$ cm^{-1}) **in minerals**

Mineral	Coordination	A	B	Mineral	Coordination	A	B
Oxides and hydroxides				**Silicates**			
Periclase	Mg–O_6	81.4	–	Forsterite	Mg–O_6	84.2	–
Mg–spinel(3)	Al–O_6?	81.1	–	Olivine	Mg–O_6	85.4	84.6
Zn–spinel(3)	Zn–O_4?	74.9	–	Talc	Mg–O_6	87.0	84.9
Brucite	Mg–$(OH)_6$	84.6	–	Chlorite	Mg–O_6	84.2	–

Mineral	Coordination	*A*	*B*	Mineral	Coordination	*A*	*B*
Brucite (10)	Mg—$(OH)_6$	85.7	84.9	Diopside	Ca, Mg, Fe—O_6	89.4	—
Carbonates				Tremolite	Ca, Mg—O_6	87.0	85.4
Calcite	Ca—O_6	87.7	87.0	Actinolite	Ca, Mg, Fe—O_6	89.7	88.5
(3)	Ca—O_6	87.8	86.7	Wollastonite	Ca—O_6	87.6	—
Aragonite	Ca—O_9	88.0	—	Vesuvianite	Ca—O_8	88.8	—
Dolomite (11)	Ca, Mg—O_6	87.7	88.6	Oligoclase	Na, Ca—O_9	89.8	—
Magnesite (11)	Mg—O_6	86.3	87.3	Apophyllite	Ca—O_7	84.9	—
Breinerite (11)	Mg, Fe—O_6	87.8	—	Melilite	Ca—O_8?	84.1	82.9
Ankerite (11)	Ca, Mg, Fe—O_6	86.3	—	Melilite	Mg—O_4?		
Tungstates				Spodumene	Al—O_6	80.2	—
Scheelite	Ca—O_8	88.6	—	Beryl	Al—O_6	84.2	—
(12)	Ca—O_8	89.5	88.9	Lepidolite	Al—O_6	88.1	—
Phosphates				**Titanosilicates**			
Apatite	Ca—O_7	90.0	88.9	Sphene	Ca—O_7	89.9	—
(13)	Ca—O_7	90.2	87.4	**Borosilicates**			
Borates				Datolite	Ca—O_8	88.8	—
Ascharite	Mg—O_6	86.6	—	**Sulfides**			

Hydroboracite	Ca–O_8	90.0	–	Sphalerite	Zn–S_4	64.1

radical cations. Taking into account that the state of the bond is very close to the state of the bond of the cation replaced by manganese, one may suppose that these data make it possible to judge the degree of ionicity of the bonds of non-radical cations with oxygen in these complex compounds (see Table 3).

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Note: Figure translations are in progress. See original paper for figures.