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Hardness, isomer shifts and chemical bond properties of rare earth orthoferrites

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ABSTRACT

The chemical bond parameters of the rare earth iron orthoferrites were calculated using the chemical bond dielectric theory of complex structural crystals. The environment factor defined by electron polarizabilities and covalency was employed to calculate Mossbauer isomer shift of $REFeO_3$. The calculated isomer shift of $YFeO_3$ was in agreement with its measurement value. The hardness of $YFeO_3$ was predicted, which is also in agreement with the experimental value.

1. Introduction

Rare earth (RE) orthoferrites ($REFeO_3$) form an important class of weak ferromagnetic materials with interesting magnetic and magnetooptical properties. Orthoferrites are transparent, and can modify the polarisation of a beam of light under the control of a magnetic field, which makes them potentially useful as optical sensors and actuators. They were also applied as the magnetic material in bubble memory [1]. The sythesis, optical, mechanical and spectrum properties of orthoferrites were studied widely [2]. It is accepted generally that the chemical bonding plays the crucial roles in determining the various properties. However, the chemical bond properties of $REFeO_3$ are not studied yet. In this paper we will employ the dielectric theory of complex structure crystals to study their bonding properties, and apply the obtained chemical bond parameters to predict their hardness and Mossbauer isomer shifts.

2. Theoretical method

A chemical bond theory of complex structure crystals is proposed by Zhang [3,4]. Its crucial step is decomposing the complex crystal into pseudobinary crystals each containing only one type of chemical bond. For the multibond crystal $A_aB_b\ldots$, the subformula for any kind of chemical bond A–B can be expressed as:

$$\left[\frac{N(\mathrm{B{-}A})a}{N_{\mathrm{CA}}}\right]\mathrm{A}\left[\frac{N(\mathrm{A{-}B})b}{N_{\mathrm{CB}}}\right]\mathrm{B} \tag{1}$$

where A, B, . . . represent different elements or different sites of the same element in the crystal formula, and $a, b, \ldots$ represent numbers of the corresponding element, $N(\mathrm{B{-}A})$ represents the number of B ions in the coordination group of A ion, and N_{CA} represents the nearest coordination number of A ion. These binary crystals are related to each other, and every binary crystal includes only one type of chemical bond. However, the properties of these psuedo-binary crystals are different from those of real binary crystals, although their chemical bond parameters can be calculated in a similar way. According to Eq. (1), each type of bond has its corresponding subformula, and the sum of all subformula equals the crystal formula, which is called the bond-valence equation.

On the analogy of the work of Phillips [5], the average energy gap E_g^μ for every μ bond in the psuedobinary crystals can be separated into homopolar E_h^μ and heteropolar C^μ parts. The homopolar gap E_h^μ can be interpreted as produced by the symmetric part of the total potential, while the ionic or charge-transfer gap C^μ results from the effect of the antisymmetric part. The average valence-conduction band gap is given by

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2 \tag{2}$$

The ionicity and covalency of any type of chemical bond is defined as follows:

$$f_i^\mu = \frac{(C^\mu)^2}{(E_g^\mu)^2} \tag{3}$$

$$f_c^\mu = \frac{(E_h^\mu)^2}{(E_g^\mu)^2} \tag{4}$$

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and

$$E_{\mathrm{h}}^{\mu} = \frac{39.74}{(d^{\mu})^{2.48}}\,(\mathrm{eV}) \tag{5}$$

where d^{μ} is the bond length. For any binary crystal, i.e. AB_n type compounds, the heteropolar C^{μ} part is defined as

$$C^{\mu} = \frac{14.4b^{\mu}[(Z_{\mathrm{A}}^{\mu})^{*} + \Delta Z_{\mathrm{A}}^{\mu} - n(Z_{\mathrm{B}}^{\mu})^{*}]\ \mathrm{e}^{-k_{\mathrm{s}}^{\mu} r_0^{\mu}}}{r_0^{\mu}}\,(\mathrm{eV}) \tag{6}$$

$$r_0^{\mu} = \frac{d^{\mu}}{2}$$

$$k_{\mathrm{s}}^{\mu} = \left(\frac{4k_{\mathrm{F}}^{\mu}}{\pi a_{\mathrm{B}}}\right)^{1/2} = 1.551(k_{\mathrm{F}}^{\mu})^{1/2} \tag{7}$$

$$(k_{\mathrm{F}}^{\mu})^{3} = 3\pi^{2} N_{\mathrm{e}}^{\mu} \tag{8}$$

$$N_{\mathrm{e}}^{\mu} = \frac{(n_{\mathrm{e}}^{\mu})^{*}}{v_{\mathrm{b}}^{\mu}} \tag{9}$$

$$(n_{\mathrm{e}}^{\mu})^{*} = [(Z_{\mathrm{A}}^{\mu})^{*}/N_{\mathrm{CA}}^{\mu} + (Z_{\mathrm{B}}^{\mu})^{*}/N_{\mathrm{CB}}^{\mu}] \tag{10}$$

$$v_{b}^{\mu} = \frac{(d^{\mu})^{3}}{\sum_{\nu}[(d^{\nu})^{3} N_{b}^{\nu}]} \tag{11}$$

here v_{b}^{μ} is the bond volume, $(n_{\mathrm{e}}^{\mu})^{*}$ is the number of effective valence electrons per μ bond, N_{e}^{μ} is the number of valence electrons of μ bond per cubic centimeter. k_{F}^{μ} and k_{s}^{μ} are Fermi wave number and Thomas–Fermi screening wave number of valence electron in binary crystal composed of only one type of bond μ, respectively. a_{B} is the Bohr radius and n is the ratio of element B to element A in the subformula. $(Z_{\mathrm{A}}^{\mu})^{*}$ and $(Z_{\mathrm{B}}^{\mu})^{*}$ are the number of effective valence electrons of the A and B ions, respectively, and $(Z_{\mathrm{A}}^{\mu})^{*} = Q_{\mathrm{AB}}^{\mu} \cdot N_{\mathrm{CA}}^{\mu}$, $(Z_{\mathrm{B}}^{\mu})^{*} = [(Q_{\mathrm{AB}}^{\mu} \cdot N_{\mathrm{CB}}^{\mu})/(8 - Z_{\mathrm{B}}^{\mu})] \cdot Z_{\mathrm{B}}^{\mu}$, Q_{AB}^{μ} is Pauling bond valence of A–B bonds, Z_{B}^{μ} is the number of valence electrons of the B atoms. $\Delta Z_{\mathrm{A}}^{\mu}$ is correction factors from d electron effects such as the crystal field stable energy and Janh-Teller effect [6,7]. b^{μ} is proportional to the square of the average coordination number N_{c}^{μ}

$$b^{\mu} = \beta(N_{\mathrm{c}}^{\mu})^{2} \tag{12}$$

$$N_{\mathrm{c}}^{\mu} = \frac{N_{\mathrm{CA}}^{\mu}}{1+n} + \frac{nN_{\mathrm{CB}}^{\mu}}{1+n} \tag{13}$$

where b^{μ} depends on a given crystal structure. The typical value of β is $0.089 \pm 10\%$ [8].

If the dielectric constant of the crystal is known, the value of β can be deduced from the Kramers–Kronig relation of dielectric function at the long wave limit, which is written as

$$\chi^{\mu} = [(4\pi N_{\mathrm{e}}^{\mu} e^{2}/m) D^{\mu}/(E_{\mathrm{g}}^{\mu})^{2}](1 - E_{\mathrm{g}}^{\mu}/4E_{\mathrm{F}}^{\mu} + (E_{\mathrm{g}}^{\mu})^{2}/48(E_{\mathrm{F}}^{\mu})^{2}) \tag{14}$$

$$\varepsilon(\infty) = 1 + \chi = 1 + \sum_{\mu} F^{\mu} \chi^{\mu} \tag{15}$$

where χ is the macroscopic linear susceptibility, χ^{μ} is the total macroscopic susceptibility of a binary crystal composed of only one type of bond μ, E_{F}^{μ} is Fermi energy, F^{μ} is the fraction of the binary crystal composing the actual complex crystal. D^{μ} is periodic dependent constants tabulated in Ref. [8].

3. Results and discussion

The orthoferrite $REFeO_3$ (RE = rare earth or yttrium) crystallizes in a distorted perovskite structure with an orthorhombic unit cell. The space group is *Pbmn*. There are four formula units in per cell. In $REFeO_3$, the coordination number of RE is 8, Fe is 6, O(1) is 5, O(2) is 4. The structure of $REFeO_3$ is shown in Fig. 1.

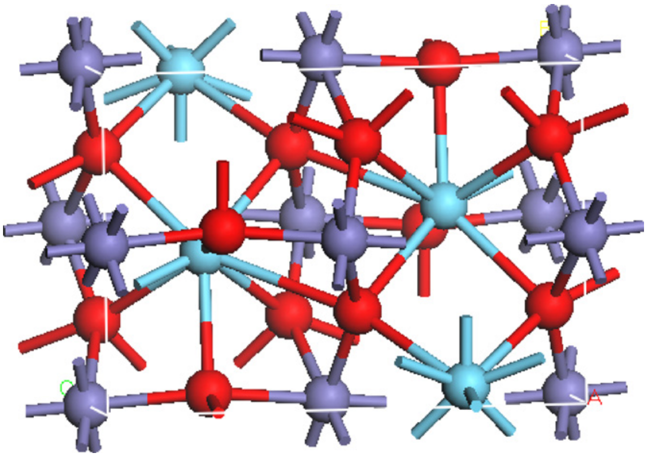

Fig. 1. Crystal structure of $REFeO_3$.

According to theory [3,4], the crystal formula of $YFeO_3$ can be converted into a subformula equation as follows:

$$YFeO_3 = 3/4YO(1)_{8/5} + 1/4YO(2)_{2} + 2/3FeO(1)_{6/5} + 1/3FeO(2)_{3/2} \tag{16}$$

$YFeO_3$ is distorted perovskite structure crystal, and contain 8 type of chemical bonds depending on bond lengths and sites. There are 14 bonds in a unit cell in total: 2 $YO(1)_{8/5}$ (d = 2.404 Å), 2 $YO(1)_{8/5}$ (d = 2.447 Å), 2 $YO(1)_{8/5}$ (d = 2.755 Å), 1 $YO(2)_2$ (d = 2.320 Å), 1 $YO(2)_2$ (d = 2.532 Å), 2 $FeO(1)_{6/5}$ (d = 1.914 Å), 2 $FeO(1)_{6/5}$ (d = 2.040 Å), and 2 $FeO(2)_{3/2}$ (d = 1.931 Å). Here we try to determine Pauling bond valence by Mulliken overlap populations for each kind of bond.

$$Q_{\mathrm{AB}}^{\mu} = \frac{Z_{\mathrm{A}} \cdot P_{\mathrm{AB}}}{\sum_{\nu} P_{\mathrm{A}\nu}} \tag{17}$$

where Q_{AB}^{μ} is Pauling bond valence of A–B bonds. Z_{A} are the valence of cation A. P_{AB} is the Mulliken overlap population of A–B bond. Therefore, a first-principles calculation was employed using an ultrasoft pseudopotential method as implemented in CASTEP [9] to obtain the Mulliken overlap populations for each kind of bond.

The refractive index, n, at 1.6 μm of $YFeO_3$ is 2.229 [10]. Using the dielectric constant of $YFeO_3$, $\varepsilon = n^2 = 4.96$, the value of β deduced from the Kramers–Kronig relation of dielectric function is 0.076. And we calculate detailed bond parameters and linear optical susceptibilities of individual bonds. These results are listed in Table 1. Using the β value of $YFeO_3$ the bond parameters of other $REFeO_3$ are also estimated (see Table 2).

Using the calculated chemical bond parameters we can employ the chemical bond theory of hardness to predict hardness of these materials. The hardness of psuedobinary compound composed of μ-type bond can be calculated as follows [11,12]:

$$\begin{aligned} H_{\mathrm{v}}^{\mu}\,(\mathrm{GPa}) &= 8.82(N_{\mathrm{e}}^{\mu})^{2/3} E_{\mathrm{h}}^{\mu}\ \mathrm{e}^{-1.191 f_{\mathrm{i}}^{\mu}} \\ &= H_{\mathrm{v}}^{\mu} = 350(N_{\mathrm{e}}^{\mu})^{2/3}\ \mathrm{e}^{-1.191 f_{i}^{\mu}}/(d^{\mu})^{2.5} \end{aligned} \tag{18}$$

The average hardness H_{ν} of complex crystals may be calculated by a geometric average of all bonds as follows:

$$H_{\mathrm{v}} = \Big[\prod^{\mu} (H_{\mathrm{v}}^{\mu})^{n^{\mu}}\Big]^{1/\Sigma n^{\mu}} \tag{19}$$

where n^{μ} is the number of bond of type μ composing the actual complex crystal. As shown in Table 1, our calculated values of average hardness for $YFeO_3$, 10 GPa, is in good agreement with the available experimental one [13].

Table 1
Chemical bond parameters and hardness of $YFeO_3$. $H_{v\,av.}$ and $H_{v\,exp.}$ are calculated and experimental Vickers hardness, respectively. Q^{μ}_{AB} is Pauling bond valence of A–B bonds. P_{AB} is the Mulliken overlap population of A–B bond.

Bond type	P_{AB}	Q^{μ}_{AB}	d^{μ} (Å)	v^{μ}_{b} (Å^3)	N^{μ}_{e} (Å^{-3})	ΔZ^{μ}_{A}	E^{μ}_{h} (eV)	E^{μ}_{g} (eV)	f^{μ}_{i}	χ^{μ}	H^{μ}_{v}	$H_{v\,av.}$ (GPa)	$H_{v\,exp.}$ (GPa)
YO1	0.24	0.493	2.404	4.534	6.154	0.000	4.513	16.273	0.923	2.162	7.471	10.0	10.17 [13]
YO1	0.28	0.575	2.447	4.781	6.154	0.000	4.319	16.774	0.934	2.267	7.548		
YO1	0.06	0.123	2.755	6.824	6.154	0.000	3.219	6.148	0.726	2.388	2.031		
YO2	0.14	0.288	2.320	4.075	5.333	0.000	4.930	10.700	0.788	3.328	7.191		
YO2	0.16	0.329	2.532	5.297	5.333	0.000	3.969	9.245	0.816	3.960	5.130		
FeO1	0.35	0.559	1.914	2.288	5.455	0.897	7.943	16.650	0.772	4.742	27.088		
FeO1	0.26	0.415	2.040	2.770	5.455	0.897	6.782	12.168	0.689	5.439	18.411		
FeO2	0.33	0.527	1.931	2.350	4.800	0.897	7.771	13.174	0.652	7.091	28.887		

The tendencies of hardness of $REFeO_3$ changing along the rare earth elements sequence is are monotone increasing. According theory [12], bond density or electronic density, bond length and degree of covalent bonding are three determinative factors for the hardness of a crystal. From Tables 1 and 2 it can be seen that the larger the ionicity, the smaller the hardness of the pseudobinary crystals. REO bonds are of greater ionic, thus the pseudobinary crystals REO have the smaller hardness values. In contrast, FeO bonds have the smaller ionicity, thus their hardness are higher.

It has been known that the ^{57}Fe isomer shift can provide extensive and valuable information about the local chemical environment of iron. For a given oxidation state, a correlation between the isomer shift δ and the chemical environmental factor h_e is found

Table 2
Chemical bond parameters and hardness of rare earth iron orthoferrites. $H_{v\,av.}$ is calculated vickers hardness.

	Bond type	d^{μ} (Å)	v^{μ}_{b} (Å^3)	N^{μ}_{e} (Å^{-3})	E^{μ}_{h} (eV)	E^{μ}_{g} (eV)	f^{μ}_{i}	χ^{μ}	H^{μ}_{v}	$H_{v\,av.}$ (GPa)
$LaFeO_3$	LaO1	2.474	4.925	0.401	4.203	15.149	0.923	2.457	6.580	9.0
	LaO1	2.493	5.039	0.457	4.124	15.991	0.933	2.531	6.959	
	LaO1	2.839	7.442	0.066	2.988	5.733	0.728	2.693	1.773	
	LaO2	2.313	4.025	0.286	4.967	10.764	0.787	3.553	7.312	
	LaO2	2.648	6.039	0.218	3.551	8.292	0.817	4.622	4.199	
	FeO1	1.943	2.386	0.936	7.653	16.055	0.773	4.896	25.359	
	FeO1	2.095	2.991	0.555	6.349	11.420	0.691	5.728	16.339	
	FeO2	1.992	2.571	0.819	7.194	12.229	0.654	7.532	25.115	
$PrFeO_3$	PrO1	2.459	4.841	0.408	4.267	15.383	0.923	2.422	6.758	9.2
	PrO1	2.484	4.990	0.461	4.162	16.143	0.934	2.507	7.068	
	PrO1	2.821	7.309	0.067	3.035	5.819	0.728	2.660	1.824	
	PrO2	2.317	4.050	0.284	4.946	10.724	0.787	3.557	7.248	
	PrO2	2.620	5.855	0.225	3.646	8.510	0.816	4.522	4.402	
	FeO1	1.937	2.366	0.944	7.712	16.177	0.773	4.861	25.699	
	FeO1	2.083	2.942	0.564	6.440	11.579	0.691	5.662	16.761	
	FeO2	1.979	2.523	0.835	7.312	12.423	0.654	7.433	25.859	
$NdFeO_3$	NdO1	2.442	4.746	0.416	4.341	15.654	0.923	2.384	6.968	9.4
	NdO1	2.471	4.917	0.468	4.216	16.363	0.934	2.474	7.231	
	NdO1	2.801	7.162	0.069	3.090	5.917	0.727	2.624	1.883	
	NdO2	2.315	4.043	0.285	4.956	10.750	0.787	3.545	7.271	
	NdO2	2.593	5.682	0.231	3.741	8.729	0.816	4.426	4.610	
	FeO1	1.929	2.339	0.955	7.791	16.341	0.773	4.817	26.167	
	FeO1	2.070	2.891	0.574	6.541	11.754	0.690	5.590	17.235	
	FeO2	1.964	2.469	0.853	7.451	12.653	0.653	7.321	26.753	
$SmFeO_3$	SmO1	2.431	4.684	0.421	4.390	15.830	0.923	2.361	7.108	9.6
	SmO1	2.466	4.889	0.471	4.237	16.449	0.934	2.461	7.295	
	SmO1	2.787	7.058	0.070	3.128	5.986	0.727	2.600	1.927	
	SmO2	2.322	4.082	0.282	4.919	10.676	0.788	3.560	7.168	
	SmO2	2.574	5.560	0.237	3.810	8.886	0.816	4.362	4.764	
	FeO1	1.926	2.329	0.959	7.821	16.403	0.773	4.800	26.344	
	FeO1	2.062	2.859	0.581	6.604	11.863	0.690	5.549	17.537	
	FeO2	1.954	2.433	0.866	7.546	12.808	0.653	7.250	27.377	
$EuFeO_3$	EuO1	2.426	4.658	0.423	4.413	15.914	0.923	2.348	7.172	9.63
	EuO1	2.465	4.886	0.471	4.242	16.470	0.934	2.456	7.305	
	EuO1	2.780	7.009	0.070	3.148	6.022	0.727	2.586	1.948	
	EuO2	2.329	4.121	0.279	4.883	10.604	0.788	3.574	7.067	
	EuO2	2.564	5.499	0.239	3.847	8.971	0.816	4.325	4.847	
	FeO1	1.927	2.334	0.957	7.811	16.386	0.773	4.800	26.268	
	FeO1	2.059	2.848	0.583	6.628	11.906	0.690	5.529	17.646	
	FeO2	1.947	2.408	0.875	7.614	12.919	0.653	7.197	27.818	
$GdFeO_3$	GdO1	2.420	4.621	0.427	4.440	16.006	0.923	2.340	7.255	9.7
	GdO1	2.461	4.860	0.474	4.259	16.532	0.934	2.451	7.361	
	GdO1	2.773	6.953	0.071	3.167	6.056	0.726	2.578	1.972	
	GdO2	2.331	4.130	0.279	4.872	10.581	0.788	3.583	7.042	
	GdO2	2.552	5.419	0.243	3.892	9.070	0.816	4.292	4.953	
	FeO1	1.925	2.326	0.961	7.831	16.423	0.773	4.796	26.405	
	FeO1	2.054	2.826	0.587	6.668	11.972	0.690	5.511	17.853	
	FeO2	1.943	2.392	0.881	7.653	12.980	0.652	7.178	28.096	

Table 3
Relation between isomer shifts δ and h_e in $REFeO_3$. $\delta_{calc.}$ and $\delta_{exp.}$ are calculated and experimental isomer shifts with respect to α-Fe at room temperature, respectively.

	Site	h_e	$\delta_{calc.}$ (cm/s)	$\delta_{exp.}$ [16]
$YFeO_3$	Fe	0.792	0.316	0.30 ± 0.01
$LaFeO_3$	Fe	0.827	0.291	
$PrFeO_3$	Fe	0.819	0.296	
$NdFeO_3$	Fe	0.811	0.302	
$SmFeO_3$	Fe	0.806	0.306	
$EuFeO_3$	Fe	0.803	0.308	
$GdFeO_3$	Fe	0.801	0.310	

[7]. This can be written as:

$$\delta(^{57}\mathrm{Fe}) = \delta_0 + 0.7h_e\,(\mathrm{mm\ s^{-1}},\ \text{relative to } \alpha\text{-Fe at room temperature}) \tag{20}$$

where δ_0 is the isomer shift of the free-ion state. For an isolated high-spin $Fe^{3+}(d^5)$, δ_0 is 0.87 $\mathrm{mm\,s^{-1}}$.

The chemical environmental factor, h_e, can be written as [14]:

$$h_e = \left(\sum_{\mu} \alpha_L^{\mu} f_c^{\mu}\right)^{1/2} \tag{21}$$

in which α_L^{μ} is polarizability of ligand in μ bond, f_c^{μ} represents the covalency of μ bond. For the μth bond, the polarizable coefficient α_0^{μ} can be obtained from the Lorentz–Lorenz equation:

$$\alpha_0{}^{\mu} = (3/4\pi)(\varepsilon^{\mu} - 1)/(\varepsilon^{\mu} + 2) \tag{22}$$

where ε^{μ} is the low-frequency dielectric constant of a binary crystal composed of only one type of μ bond; the polarizabilities of the bond volume are

$$\alpha_b{}^{\mu} = \alpha_0{}^{\mu} V_b{}^{\mu} \tag{23}$$

and the electron polarizabilities of the ion volume in the μth bond are

$$\alpha_A^{\mu} = \{(r_A^{\mu})^3/[(r_A^{\mu})^3 + (r_B^{\mu})^3]\}\alpha_b^{\mu} \tag{24}$$

$$\alpha_B^{\mu} = \{(r_B^{\mu})^3/[(r_A^{\mu})^3 + (r_Z^{\mu})^3]\}\alpha_b^{\mu} \tag{25}$$

here r_A^{μ} and r_B^{μ} are effective radius of A and B ions [15], respectively.

The results of calculated isomer shift of $YFeO_3$ are shown in Table 3. From Table 3, it is clearly seen that the calculated results of Mossbauer isomer shifts in Fe positions are in good agreement with their experimental values. This also shows that the chemical bond parameters calculated by us are reasonable. The results of calculated isomer shifts of other rare-earth iron orthoferrites are shown in Table 3.

4. Conclusion

In conclusion, the detailed chemical bond parameters of the rare earth iron orthoferrites were calculated using the chemical bond dielectric theory of complex structural crystals. Results indicated that RE–O bonds are ionic and Fe–O bonds have higher covalency. The environment factor defined by electron polarizabilities and covalency was employed to Mossbauer isomer shift of Fe ions. The calculated isomer shift of $YFeO_3$ was in agreement with its measurement value. The hardness of $YFeO_3$ was predicted, which is also in agreement with the experimental value.

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