UDK 541.67:546.725

THEORETICAL STUDY ON MÖSSBAUER ISOMER SHIFT OF LAYERED COMPOUNDS

© 2010　L. Gao, Y. Xu, N. Qu, F. Gao*

Department of Applied Chemistry, Yanshan Univesity, Qinhuangdao 066004, P.R. China

Using the expended chemical bond dielectric theory of complex crystals, we have calculated chemical bond parameters and Mössbauer isomer shift of LnOFeAs as well as AFe_2As_2 which had been chosen due to their layered structures. Results are in good agreement with available experimental data, demonstrating the accuracy of our calculations and theories. The relationship between chemical bond parameters and Mössbauer isomer shift is discussed.

K e y w o r d s: Mössbauer isomer shift, chemical bond parameters, layered structure.

INTRODUCTION

Recently, quaternary rare earth transition metal oxypnictides with the chemical formula LnOTMPn (Ln = rare earth metal, TM = transition metal, Pn = P, As, Sb, Bi) have attracted much attention because of their superconductivity [1] and possible further raising of superconducting temperature T_c by doping with F^-, Sr^{2-}, K^+ ions and so on [2—6]. These compounds crystallize with the tetragonal ZrCuSiAs structure [7] belonging to $P4/nmm$ space group and are composed of a stack of alternant LnO and TMPn layers. The quasi-two-dimensional (2D) character, taking LaOFeAs as an example, contains multiple different chemical bonds, in which Fe—As bond is strongly covalent and relative weak ionicity is presented in La—O bonds, as well as between Fe—As layers and La—O layers. From this ionic perception, we can assume a charge transfer according to $(LaO)^+(FeAs)^-$ [8].

Another well known type of compounds is AFe_2As_2 (A = alkaline-earth metals or Eu, etc) which crystallize with the $ThCr_2Si_2$ structure, space group $I4/mmm$. These layered materials have not only the similar structure to LnOTMPn, merely the Ln—O layers substituted by A atoms, but also the remarkable alike electronic and magnetic properties, probably because of the identical Fe—As layers. Therefore, they have the most possibility to become superconductor like LnOTMPn.

Fig. 1 shows the comparison of both structures. It is a pity, however, that the final conclusion of superconducting mechanism has not been obtained, although it is believed that the doping electrons or holes may be responsible for the superconductivity and that pressure can effects the orbital degeneracy and the electron density of state at the Fermi level, which in turn induce the significant change in T_c [9]. Therefore, to date lots of researches have been conducted on the aspects of synthesis, structural analysis,
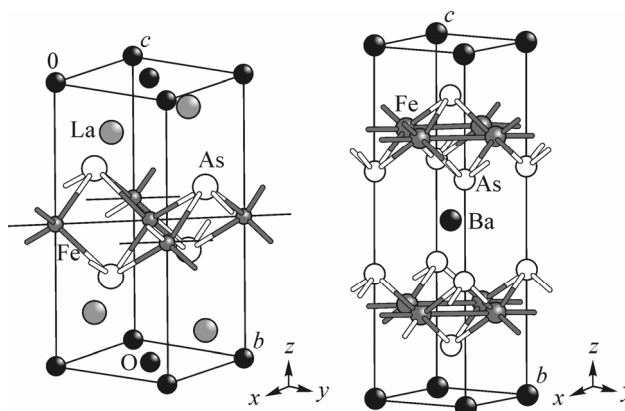

Fig. 1. The 3D pictures of LaOFeAs (*left*) and $BaFe_2As_2$ (*right*) primitive cells

* E-mail: ysuglh@163.com

T a b l e   1

The space groups and lattice parameters of layered compounds

Compound	Space group	a, Å	c, Å	c/a	Compound	Space group	a, Å	c, Å	c/a
LaOFeAs[a]	*P4/nmm*	4.038	8.753	2.168	GdOFeAs[a]	*P4/nmm*	3.915	8.435	2.155
CeOFeAs[a]	*P4/nmm*	4.000	8.655	2.164	BaFe$_2$As$_2$[b]	*I4/nmm*	3.9625	13.0168	3.285
PrOFeAs[a]	*P4/nmm*	3.985	8.595	2.157	SrFe$_2$As$_2$[c]	*I4/nmm*	3.9243	12.3644	3.151
NdOFeAs[a]	*P4/nmm*	3.965	8.575	2.163	EuFe$_2$As$_2$[c]	*I4/nmm*	3.9062	12.1247	3.104
SmOFeAs[a]	*P4/nmm*	3.940	8.496	2.156					

[a] Reference [18].
[b] Reference [19].
[c] Reference [20].

electronic and magnetic properties which are related to superconductivity potentially [10—13], whereas there are few theoretical prediction and calculation about the chemical bond properties, Mössbauer isomer shift and so on, all of which can provide a more comprehensive understanding about these two families. It is well known that Mössbauer isomer shift can be used to describe the local structure, magnetic properties, bonding of compounds, etc. More valuable information about the close environment of the Mössbauer nucleus within the structure can be obtained from the hyperfine parameters provided by isomer shift. Therefore it is meaningful to obtain the isomer shift values. What is more important is that seeking and founding a theoretical method to calculate the isomer shift value can serve as a guide in predicting the properties of new compounds whose characterizations are difficult to conduct or even those that haven′t been successfully synthesized.

The theories which were used to calculate chemical bond properties have been described in detail in many articles [14—17]. It should be noted that, however, the calculated results are in accordance with experimental values only when the theories are applied to materials with uniform structure. It fails to calculate the compounds with layered structures, like LnOFeAs. The aim of this paper is to extend the method to calculation for the Mössbauer isomer shift and related parameters of the layered compounds. We will take LnFeOAs (Ln = La, Ce, Pr, Nd, Sm, Gd) [18] for examples. To support our method, we have also calculated the properties of the typical layered compounds, BaFe$_2$As$_2$, SrFe$_2$As$_2$, EuFe$_2$As$_2$ which have different structure and space group to that of LnOFeAs. The data in Table 1 are the lattice parameters of the layered compounds mentioned above, which were used to build the molecule model with Materials Studio to measure the bond length.

THEORETICAL CALCULATION OF THE MÖSSBAUER SHIFT

^{57}Fe is one of the most important Mössbauer elements and the relationship between isomer shift (δ) and chemical environmental factor (h) has been determined as follows [21]:

$$\delta = \delta_0 - 0.7h \tag{1}$$

$$h = (\sum_{\mu} \alpha_L^\mu f_c^\mu)^{1/2} \tag{2}$$

in which α_L^μ is polarizability of ligand in μ bond, f_c^μ represents the covalency of μ bond, and δ_0 is the isomer shift of Fe^{n+}. For Fe^{2+} and Fe^{3+}, δ_0 are 1.68 and 0.87, respectively.

The polarizability of central ion and ligand ion in μ bond can be calculated as follows:

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

$$\alpha_B^\mu = \{(r_B^\mu)^3 / [(r_A^\mu)^3 + (r_B^\mu)^3]\}\alpha_b^\mu \tag{4}$$

here r_A^μ and r_B^μ are effective radius of A and B ions, respectively, r_b^μ denotes the polarizability of bond volume which can be obtained by formulae (5) and (6):

$$\alpha_b^\mu = \alpha_0^\mu V_b^\mu \tag{5}$$

$$\alpha_0^\mu = (3/4\pi)(\varepsilon^\mu - 1)/(\varepsilon^\mu + 2). \tag{6}$$

V_b^μ is bond volume of μ bond, which can be defined by the following equation based on the Levine theory:

$$V_b^\mu = \frac{(d^\mu)^3}{\sum_\nu N_b^\nu (d^\nu)^3}. \tag{7}$$

N_b^ν is bond density, i.e. the number of ν bond in 1cm^3. ε^μ is dielectric constant:

$$\varepsilon^\mu = 1 + \chi^\mu \tag{8}$$

$$\chi^\mu = (h\Omega_P^\mu)^2 / (4\pi E_g^\mu)^2 \tag{9}$$

where χ^μ is electric polarizability, Ω_P^μ is plasma frequency, and E_g^μ represents the average energy gap of each μ-type bond, which can be separated into homopolar gap E_h^μ and heteropolar C^μ parts, and the relationship can be expressed as follows:

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2 \tag{10}$$

$$E_h^\mu = 39.74 / (d^\mu)^{2.48} \tag{11}$$

$$C^\mu = 14.4 b^\mu [(Z_A^\mu)^* + \Delta Z_A^\mu - n(Z_B^\mu)^*] e^{-k_s^\mu r_0^\mu} / r_0^\mu \tag{12}$$

$$r_0^\mu = d^\mu / 2 \tag{13}$$

$\exp(-k_s^\mu \cdot r_0^\mu)$ is the Thomas-Fermi shielding factor. ΔZ_A^μ is a correction factor from d electron effects.
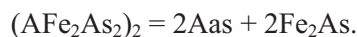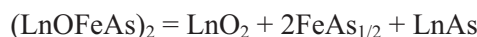
Based on the values of homopolar gap E_h^μ and heteropolar C^μ, we can easily get the ionicity f_c^μ and covalency f_c^μ values of μ-type chemical bond:

$$f_i^\mu = (C^\mu)^2 / (E_g^u)^2 \tag{14}$$

$$f_c^\mu = (E_h^\mu)^2 / (E_g^\mu)^2. \tag{15}$$

The chemical bond properties and isomer shift of the crystal can be obtained according to formulae (1) ~ (15).

First of all, the crystal should be decomposed into different kinds of pseudo-binary crystals based on the theories described in Ref 15—17 and then the properties of each bond can be calculated. The decompositions of LnOFeAs ($Z = 2$) and AFe_2As_2 ($Z = 2$) into the sum of pseudo-binary crystals are given as follows:

$$(LnOFeAs)_2 = LnO_2 + 2FeAs_{1/2} + LnAs$$

$$(AFe_2As_2)_2 = 2Aas + 2Fe_2As.$$

Then we calculated the chemical bond properties and isomer shift of the crystals above mentioned and found that the results had significant error when compared with experimental data. The reason may be that some formulae are unsuitable to apply on crystals with layered structure, especially the bond volume (V_b) which is closely related with crystal structure. So we bring forward a new method to improve it, and the expression is shown as follows:

$$V_b(\text{La—O}) = \frac{2l_1}{c} \times V \times \frac{1}{n_{\text{La—O}}}, \tag{16}$$

$$V_b(\text{La—As}) = \frac{2l_2}{c} \times V \times \frac{1}{n_{\text{La—As}}}, \tag{17}$$
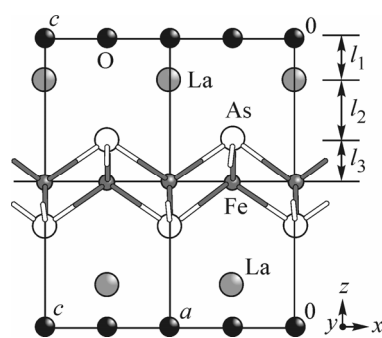
Fig. 2. The sheme of layered structure partition

$$V_b(\text{Fe—As}) = \frac{2l_3}{c} \times V \times \frac{1}{n_{\text{Fe—As}}}, \qquad (18)$$

here c is the unit cell parameter, V represents the unit cell volume and n is the number of μ type bond. l_1, l_2, l_3 are thickness of La—O, La—As, Fe—As layers along c-axis, respectively, which are shown in Fig. 2. The sum of l_1, l_2 and l_3 is equal to half of c because Fe layer is exactly in the middle of unit cell.

RESULTS AND DISCUSSION

The chemical bond properties and isomer shift of LnOFeAs (Ln = La, Ce, Pr, Nd, Sm, Gd) have been calculated and presented in Table 2. To support our method, we have also calculated the isomer shift of typical layered compounds $BaFe_2As_2$, $SrFe_2As_2$, $EuFe_2As_2$, which have different structure and space group to that of LnOFeAs.

Since there have been detailed information about isomer shift of the mentioned compounds [8, 20, 22], we just focus our discussion on the relationship between isomer shift and chemical bond properties in this paper. From Table 2 we can see that a good agreement between the calculated results and available experimental ones is observed, which demonstrates the accuracy of our calculations and theories that have been modified so as to be more suitable for the layered materials.

The data in Table 1 show that the lattice parameters are decreasing with the decrease of rare earth and Ba, Sr, Eu ionic radii. Moreover, the compression in c-axis is a little stronger than in a-axis on the whole. This anisotropic deformation of the crystal structure is caused by strong anisotropy of interatomic bonds, that′s to say, the bonds inside the Fe—As layers is stronger than relatively weak ionic coupling between adjacent Fe—As layers and La—O layers or (Ba, Sr, Eu) atomic sheets [23]. This characteristic causes the bond length of Fe—As to become shorter, which in turn decreases the thickness of Fe—As layers, and meantime generates an increase in isomer shift. According to formula (1) and (2), the isomer shift of Fe^{n+} is considered as the function of environmental factor (h) which is closely related to the covalency (f_c^μ) and polarizability (α_L^μ) of ligand in μ bond. From Table 2 we

T a b l e 2

The chemical bond properties and isomer shift which are obtained at 298 K *of layered crystals*

Compound	Space group	Bond type	d^μ, Å	V_b, Å^3	E_g^μ, eV	f_c^μ	α_L^μ	δ_{cal}, mm/s	δ_{exp}, mm/s
LaOFeAs	*P4/nmm*	Fe—As	2.412	5.377	5.038	0.786	0.998	0.440	0.45[a]
CeOFeAs	*P4/nmm*	Fe—As	2.416	5.418	4.737	0.786	1.005	0.435	
PrOFeAs	*P4/nmm*	Fe—As	2.404	5.339	4.800	0.786	0.988	0.447	
NdOFeAs	*P4/nmm*	Fe—As	2.394	5.274	4.673	0.785	0.973	0.456	
SmOFeAs	*P4/nmm*	Fe—As	2.377	5.160	4.759	0.784	0.948	0.472	
GdOFeAs	*P4/nmm*	Fe—As	2.361	5.058	4.842	0.784	0.926	0.487	
$BaFe_2As_2$	*I4/nmm*	Fe—As	2.403	5.339	4.757	0.9021	1.028	0.332	0.31[b]
$SrFe_2As_2$	*I4/nmm*	Fe—As	2.388	5.236	4.832	0.9018	1.005	0.347	0.31[c]
$EuFe_2As_2$	*I4/nmm*	Fe—As	2.382	5.203	4.863	0.9016	0.984	0.361	0.43[a]

[a] Represent References [22].
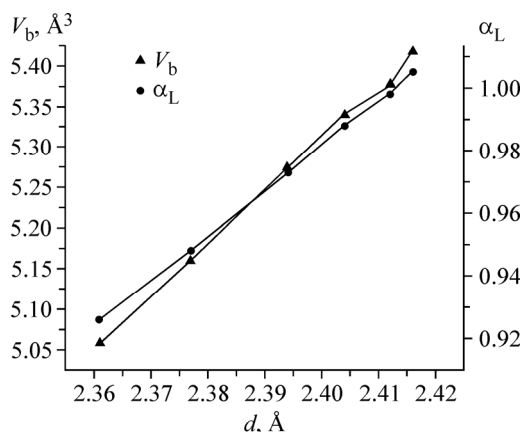[b] Represent References [8].
[c] Represent References [20].

Fig. 3. The trend of bond volume and polarization changing with the bond length
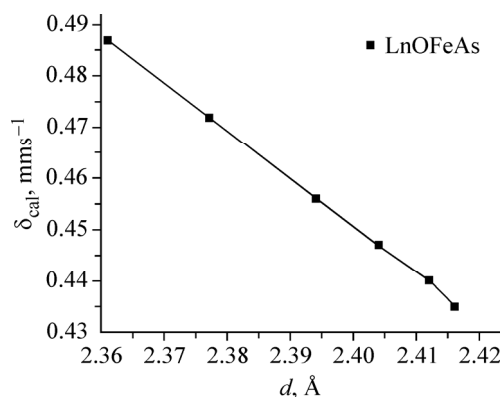

Fig. 4. The trend of isomer shift changing with the bond length

can see that, both f_c^μ and α_L^μ, as well as the bond volume (V_b), have changed along with the decrease of the bond length for these two series of compounds, i.e., a gradual decrease of Fe—X bonds length leads to a decrease in the bond volume and polarizability of ligand. Although the covalency almost remain unchanged, the decrease in these three parameters still cause a decrease in environmental factor h, which at last bring about an increase in the isomer shift. Actually, as we all known, the isomer shift is directly connected with the electron charge density inside the nucleus and the change in nuclear radius. Since the change in nuclear radius is the same for series of compounds mentioned in our paper, the electron charge density takes full responsibility for the variation in isomer shift. In our opinion, a short bond length would lead to a small bond volume and polarization, and may result in a small electron density and a relative large isomer shift value. Fig. 3 and Fig. 4 display the trend of bond volume, polarization and isomer shift changing with the bond length, which can be used to predict the variation of isomer shift and chemical bond properties for compounds with similar structures.

Another possible reason for the variation of isomer shift is the ion radii of Ln^{3+} and A^{2+}. The ion radii are decreasing from Ce^{3+} to Gd^{3+} and Ba^{2+} to Eu^{2+}, while the electron-withdrawing ability is increasing, and that may make a weak contribution to the decrease of electron density at the iron nucleus and finally an increase in the isomer shift. In summary, the variation of isomer shift is the combined action of bond length, polarization and ion radii.

It should be noted that this semiempirical model is more suitable for the chemical bond parameters and isomer shift calculations of layered compounds. That′s because the characteristics of the compounds with layered structure, taking LaOFeAs as an example, mainly arise from La—O layers and Fe—As layers which contain more bonds and less from La—As layers where there are almost no bond formations. When the formula of bond volume (V_b) is revised, the ratio of volume of containing more bonds to unit cell volume is increased, as well as the influence of properties of these layers on the macroscopic characteristics, and that can facilitate a better interpreting for the macroscopic characteristics from the chemical bond viewpoint.

CONCLUSION

In this paper, we brought forward a modified method to calculate the isomer shift of layered compounds and the isomer shift values of LnOFeAs (Ln = Ce, Pr, Nd, Sm, Gd) and AFe_2As_2 (A = Ba, Sr, Eu) have been calculated. The results indicate a relationship between bond length, bond volume, polarization, isomer shift; namely, a short bond length would lead to a small bond volume and polarization, which in turn result in a large isomer shift value. The good agreement between calculation results and available experimental data demonstrates the accuracy of our present theories. The semiempirical model can be employed to other series of complex compounds with similar layered structure. Moreover, it will provide comprehensive information from chemical bond viewpoint for layered materials,

such as the influence of change in chemical bond parameters on the macroscopic characteristics and so as to predict some properties for new compounds.

REFERENCE

1. *Takahashi H., Igawa K., Arii K. et al.* // Nature. – 2008. – **453**. – P. 376 – 378.
2. *Kamihara Y., Watanabe T., Hirano M. et al.* // J. Amer. Chem. Soc. – 2008. – **130**, N 11. – P. 3296 – 3297.
3. *Wen H.H., Mu G., Fang L. et al.* // Europhys. Lett. – 2008. – **82**. – P. 170091 – 170095.
4. *Ren Z.A., Yang J., Lu W. et al.* // Ibid. – P. 570021 – 570022.
5. *Ren Z.A., Che G.C., Dong X.L. et al.* // Ibid. – **83**. – P. 170021 – 170024.
6. *Cheng P., Fang L., Yang H. et al.* // Sci. China, Ser. G. – 2008. – **51**, N 6. – P. 719 – 722.
7. *Johnson V., Jeitschko W.J.* // Solid State Chem. – 1974. – **11**, N 2. – P. 161 – 166.
8. *Rotter M., Tegel M., Johrendt D.* // Phys. Rev. B. – 2008. – **78**. – P. 0205031 – 0205034 (R).
9. *Lu W., Shen X.L., Yang J. et al.* // Solid State Commun. – 2008. – **148**, N 3-4. – P. 168 – 170.
10. *Mcguire M.A., Christianso A.D., Sefat A.S. et al.* // Phys. Rev. B. – 2008. – **78**. – P. 09451701 – 09451710.
11. *Giovannetti G., Kumar S., Den Brink J.V.* // Phys. B. – 2008. – **403**, N 19-20. – P. 3653 – 3657.
12. *Yamamoto A., Jiang J., Tarantini C. et al.* // Appl. Phys. Lett. – 2008. – **92**. – P. 2525011 – 2525013.
13. *Yin Z.P., Lebegue S., Han M.J. et al.* // Phys. Rev. Lett. – 2008. – **101**, N 4. – P. 047001 – 047004.
14. *Zhang S.Y., Chin.* // J. Chem. Phys. – 1991. – **4**, N 2. – P. 109 – 115.
15. *Gao F.M., He J.L., Wu E.D. et al.* // Phys. Rev. Lett. – 2003. – **91**, N 1. – P. 155021 – 1550214.
16. *Gao F.M.* // Phys. Rev. B. – 2004. – **69**, N 9. – P. 09411311 – 0941136.
17. *Gao F.M., Rui X., Liu K.* // Ibid. – 2005. – **71**, N 5. – P. 0521031 – 0521034.
18. *Quebe P., Terbüchte L.J., Jeitschko W.* // J. Alloys Compd. – 2000. – **302**. – P. 70 – 74.
19. *Huang Q., Qiu Y., Bao W. et al.* // Phys. Rev. Lett. – 2008. – **101**, N 25. – P. 2570031 – 2570034.
20. *Tegel M., Rotter M., Weiß V. et al.* // J. Phys.: Condens. Matter. – 2008. – **20**. – P. 4522011 – 4522015.
21. *Gao F.M., Li D.C., Zhang S.Y.* // Ibid. – 2003. – **15**. – P. 5079 – 5084.
22. *Raffius H., Moersen E., Mosel B.D. et al.* // J. Phys. Chem. Solids. – 1993. – **54**, N 2. – P. 135 – 144.
23. *Shein I.R., Ivanovskii A.L.* // Scripta Materialia. – 2008. – **59**, N 10. – P. 1099 – 1102.