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DETERMINATION OF THE Mn^{2+}-F^- BOND LENGTH USING A COMPLETE SPECTRUM CRITERION AND A NEXT NEAREST NEIGHBOR MODEL*

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A complete spectrum criterion and a next nearest neighbor model are proposed. Research indicates: 1) Using this criterion can remove the long existing puzzle that different parameters produce different bond lengths. The criterion greatly improve the reliability of optical method for determining the Mn^{2+}-F^- distance R. 2) The exponent n and coefficient K in the inverse power law $10Dq = KR^{-n}$ are obviously affected by next nearest neighbor. 3) Considering the effect can lead to a better result, the next nearest neighbor model is thus more strict and reliable.

PACC: 6160; 6170R; 7110

I. INTRODUCTION

It is known that when a transition metal ion, as an impurity, exists in a host lattice, the distance R between this metal ion and its nearest neighbors (NN) is different from the bond length R_0 of the host lattice. To determine the real bond length is still a fundamental and difficult task which has attracted special notice.[1−5] In order to obtain the Mn^{2+}-F^- distance (bond length) R in cubic fluoroperovskite lattices, the inverse power law $10Dq = KR^{-n}$ in crystal-field theory can be used.[1,3,6] Here the exponent n and coefficient K are constants when R varies between $R - \delta R$ and $R+\delta R$, δR being equal to 0.01 nm, while the cubic field splitting parameter $10Dq$ can be derived by fitting of the optical spectrum. In Ref.[3] a linear regression was used to achieve the values of n and K, then the bond length R in $KMgF_3$:Mn^{2+}, $KZnF_3$:Mn^{2+} and $RbCdF_3$:Mn^{2+} was obtained by using equation $10Dq = KR^{-n}$. Since $10Dq$ was fitted from the optical spectrum, this method was named the optical method.[3]

However, there are two problems that should be solved when using the inverse power law to calculate R. First, in crystal-field theory, different electrostatic parameters B and C, different Trees' correction α and Racah correction β[7] can be chosen for a given optical spectrum. These different values of B, C, α, and β will cause different $10Dq$, and finally cause different values of R by the inverse power law. This is a puzzle not having been solved for a long period. Second, there is a simple model in crystal-field theory, in which the influences of the center metal ions (CMI), nearest neighbors (NN), and next nearest neighbors (NNN) on the exponent n can all be ignored. Thus for any CMI, NN and NNN, the values of n are always assumed close to 5. Such a proximity is very rough. Reference [3] also pointed out clearly that "this proximity to the values $n = 5$ predicted by crystal-field theory should be regarded as accidental." In fact, some authors pointed out that even if the influence of NNN on the exponent n is ignored, different CMI or NN will also lead to different n (see Table 1). This proximity can be called NN model. Therefore, it is unsatisfactory that up to now no work has ever reported how the exponent n changes when considering the influence of NNN.

Table 1. Different CMI, NN, and their corresponding exponent n.

CMI+NN	NiF_6^{4-}	VF_6^{4-}	CrF_6^{3-}	CrF_6^{4-}	MnF_6^{4-}	MnF_6^{4-}	MnF_6^{4-}
n	4.8[8]	5.5[8]	1.6[9]	3.2[9]	4.7[1]	4.45[3]	3.6[6]

In the present work we will propose a complete spectrum criterion to solve the first problem and a NNN model to answer the second one.

II. THE COMPLETE SPECTRUM CRITERION

The optical spectra of fluoroperovskite lattices ($KMnF_3$, $KZnF_3$:Mn^{2+}, $KMgF_3$:Mn^{2+}, $RbMnF_3$, and

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$RbCdF_3$:Mn^{2+}) have been measured as in Refs.[1,3 and 10]. The first six crystal field peaks in the excitation spectra of the above five perovskites have been assigned to the transitions from $^6A_1(S)$ to $^4T_1(G)$, $^4T_2(G)$, $^4A_1(G)$, $^4E(G)$, $^4T_2(D)$, $^4E(D)$, and $^4T_1(P)$, respectively. According to the crystal-field theory, we can fit the peak positions by selecting different B, C, α, β and corresponding $10Dq$ to diagonalize the crystal field energy matrices.[1−5,10] For instance, in order to fit the peak positions of the optical spectrum of $RbMnF_3$ at room temperature, Ref.[10] chose $B = 700\,\mathrm{cm}^{-1}$, $C = 3650\,\mathrm{cm}^{-1}$, $\alpha = \beta = 0$; while Ref.[11] chose $B = 857.41\,\mathrm{cm}^{-1}$, $C = 3080.48\ \mathrm{cm}^{-1}$, $\alpha = 61.18\,\mathrm{cm}^{-1}$ and $\beta = -123.3\,\mathrm{cm}^{-1}$. Hence these different B, C, α, and β lead to different $10Dq$ values.[3,10,11] In addition, just as pointed out in Ref.[3], even if for the same values of B, C, α, and β, the $10Dq$ selected manually by fitting still has an uncertain area of $\pm 60\,\mathrm{cm}^{-1}$. So it is considered to be impossible to get the same R value from different $10Dq$. Here we propose a complete optical spectrum criterion which can be stated as below: The best $10Dq$ value can minimize a deviation σ in fitting of peak positions for a given optical spectrum. To compare with the results in Ref.[3], the deviation σ can be written as

$$\sigma = \left[\frac{1}{N-P}\sum_i (E_i^F - E_i^D)^2\right]^{1/2},$$

where E_i^D and E_i^F correspond to the peak positions given by experiment and fitting respectively, P is the number of free parameters ($B, C, 10Dq$) and N is the number of peaks of the optical spectrum. What should be noticed is that for any set of B, C, α and β values there is only one $\sigma_{\min}$. Only the $10Dq$ corresponding to the $\sigma_{\min}$ is the best value. Although in Ref.[3] the authors used σ in fitting, they did not use the $\sigma_{\min}$ to search for the best $10Dq$. For example, in fitting of the peak positions of the optical spectrum of $KMnF_3$, the value of $10Dq = 7855\,\mathrm{cm}^{-1}$, which was manually chosen by the authors of Ref.[3], was not the best value, because the corresponding $\sigma = 250\,\mathrm{cm}^{-1}$ was not the minimum value. Our calculation found that under the same case the $\sigma_{\min}$ should be $243\,\mathrm{cm}^{-1}$ and the corresponding best $10Dq$ value should be $7775.4\,\mathrm{cm}^{-1}$. The two $10Dq$ values have a difference of about $\pm 80\,\mathrm{cm}^{-1}$, it goes beyond the uncertain range of $\pm 60\,\mathrm{cm}^{-1}$ (coming from manually choosing in Ref.[3]). Calculation in this paper has found that when using criterion rather than manually choosing $10Dq$ value, the uncertain range of $10Dq$ was only $\pm 0.1\,\mathrm{cm}^{-1}$.

Ⅲ. NNN MODEL

According to NN model used in Ref.[3], the exponent n is the same for the cubic perovskites $KMnF_3$ and $RbMnF_3$ since their CMI are all Mn^{2+} while their NN are all F^- though their NNN are different from each other (the former is K^+ and the latter is Rb^+). The crystal structure of $KMnF_3$ and $RbMnF_3$ shown in Fig.1 indicates that the NNN of Mn^{2+} in $KMnF_3$ are eight K^+ ions and in $RbMnF_3$ are eight Rb^+ ions.

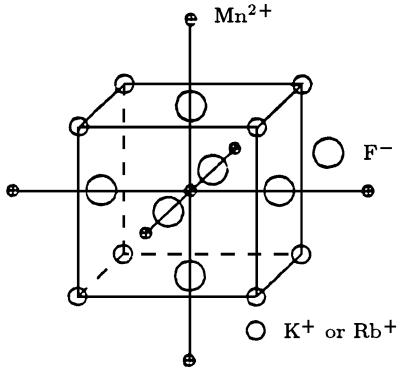


Fig.1. Structure of $KMnF_3$ and $RbMnF_3$.

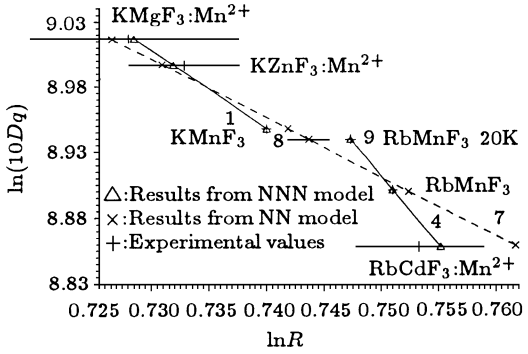


Fig.2. Plot of $\ln(10Dq)$ vs $\ln R$. Horizontal line 8 refers to R—value derived by NN model for $RbMnF_3$ at 20 K; short horizontal line 9 refers to experimental value.

For the cubic symmetry, the distance of Mn^{2+}-K^+ or Mn^{2+}-Rb^+ is only $\sqrt{3}$ times R (the Mn^{2+}-F^- distance). Hence there should exist strong interaction between CMI and NNN. In fact, only when the effect of NNN on CMI is ignored completely, can the two materials have the same n. Thus the NN model is not very strict and a further investigation is necessary. Here we propose a NNN model: Only in the same kind of materials that have equal CMI, NN and NNN, are the exponent n and the coefficient K the same. Such proximity is more strict than in the NN model. It not only admits the existence of influence of CMI and NN on n, but also shows that the influence of NNN is not negligible.

Ⅳ. CALCULATIONS

Based on crystal field theory, in the fittings 1–6 we calculated the peak positions of the optical spectra of $KMnF_3$, $KZnF_3$:Mn^{2+}, $KMgF_3$:Mn^{2+}, $RbMnF_3$, and $RbCdF_3$:Mn^{2+} at room temperature (RT) and $RbMnF_3$ at 20 K. In the fittings 1 and 4, the parameters $B = 834\,cm^{-1}$ and $C = 3094\,cm^{-1}$ were chosen while $\alpha = 65\,cm^{-1}$ and $\beta = -131\,cm^{-1}$ came from Ref.[3 and 12]. Such a set of B, C, α, β values made the corresponding σ_{min} smaller than that obtained by other sets. The B, C, α, and β used in fittings 2 and 5 were taken from Ref.[11] and those in fittings 3 and 6 came from Ref.[10]. The values of $10Dq$, σ_{min}, and the peak positions caluclated for the six peaks obtained by the present criterion are listed in Table 2.

Table 2. Experimental and fitting energies of the crystal-field peaks for $KMgF_3$:Mn^{2+}, $KZnF_3$:Mn^{2+}, $KMnF_3$, $RbMnF_3$ and $RbCdF_3$:Mn^{2+} at RT and 20 K.

	B	C	$10Dq$	σ	$^4T_1$(G)	$^4T_2$(G)	$^4A_1$(G)	$^4T_2$(G)	^4E(D)	$^4T_1$(P)
$KMgF_3$:Mn^{2+}	(0.2070 ± 0.0020)nm[1,12]									
Expt.[1]					18240	22690	25200	28070	30230	32590
Fitting 1	834	3094	8240.2	297	18421	22767	25110	28240	30038	32981
Fitting 2	857.41	3080.48	8333.9	435	18422	22864	25200	28495	30345	33147
Fitting 3	700	3650	8290.1	1604	19559	22914	25250	28367	30150	35006
$KZnF_3$:Mn^{2+}	(0.208 ± 0.0010)nm[3,12]									
Expt.[3]					18530	22830	25210	28180	30080	32750
Fitting 1	834	3094	8078.0	114	18576	22866	25110	28271	30038	32875
Fitting 2	857.41	3080.48	8171.0	314	18577	22962	25200	28527	30345	33041
Fitting 3	700	3650	8090.0	1431	19743	23034	25250	28405	30150	34888
$KMnF_3$	0.2095 nm[3,13]									
Expt.[3]					18900	23120	25245	28200	30150	32550
Fitting 1	834	3094	7695.8	141	18938	23090	25110	28347	30038	32622
Fitting 2	857.41	3080.48	7789.1	298	18939	23183	25200	28606	30345	32786
Fitting 3	700	3650	7660.0	1409	20135	23283	25250	28491	30150	34628
$RbMnF_3$	20 K (0.2111 ± 0.0001)nm[13]									
Expt.[10]					19160	23090	25376	28210	30250	32730
Fitting 4	834	3094	7633.0	250	18998	23125	25110	28360	30038	32580
Fitting 5	857.41	3080.48	7725.1	289	19000	23219	25200	28621	30345	32743
Fitting 6	700	3650	7581.4	1250	20207	23327	25250	28508	30150	34580
$RbMnF_3$	0.2120 nm[3,13]									
Expt.[3]					19300	23310	25275	28250	30150	32360
Fitting 4	834	3094	7334.2	154	19280	23291	25110	28425	30038	32376
Fitting 5	857.41	3080.48	7426.0	301	19283	23383	25200	28687	30345	32538
Fitting 6	700	3650	7250.1	1373	20507	23507	25250	28580	30150	34372
$RbCdF_3$	(0.2124 ± 0.0012)nm[3,14]									
Expt.[3]					19530	23670	25230	28350	30070	32270
Fitting 4	834	3094	7048.0	178	19550	23444	25110	28490	30038	32177
Fitting 5	857.41	3080.48	7139.2	297	19553	23533	25200	28754	30345	32338
Fitting 6	700	3650	6917.0	1329	20806	23678	25250	28657	30150	34159

In fittings 1 and 4, Trees correction $\alpha = 65\,cm^{-1}$ and Racah correction $\beta = -131\,cm^{-1}$ are taken from Ref.[3]; in fittings 2 and 5, the values of B, C, α, and β are taken from Ref.[11]; in fittings 3 and 6, B, C, and α, β are taken from Ref.[10].

Using the same optical method and NN model given by Ref.[3], we obtained the values of n, K and R from the fitting 1+4 which is called Fitting 7. The results are listed under the title NN model in Table 3. Our calculation found that using the $10Dq$ value obtained from the fitting 2+5 or 3+6 can get the same R values as those obtained from the fitting 1+4. The same R values are not listed repeatedly in Table 3.

Table 3. Calculated values of n, K, and R based on different models and different fittings and experimental R-values (the unit of K is $10^4\,\mathrm{cm}^{-1}\,\mathrm{nm}$).

		NNN model			Experiments	NN model
		Fitting 1	Fitting 2	Fitting 3		Fitting 7
		$n = 5.9492$	$n = 5.8819$	$n = 6.8319$		$n = 4.3924$
		$K = 6.2685$	$K = 6.0364$	$K = 11.984$		$K = 2.0000$
		R/nm	R/nm	R/nm	R/nm	R/nm
$KMgF_3$:Mn^{2+}	RT	0.2071 ± 0.0004	0.2071 ± 0.0004	0.2071 ± 0.0004	0.2070 ± 0.0020[a]	0.2067 ± 0.0004
$KZnF_3$:Mn^{2+}	RT	0.2078 ± 0.0004	0.2078 ± 0.0004	0.2078 ± 0.0004	0.208 ± 0.001[b]	0.2076 ± 0.0004
$KMnF_3$	RT	0.2095 ± 0.0004	0.2095 ± 0.0004	0.2095 ± 0.0004	0.2095[c]	0.2099 ± 0.0004
		Fitting 4	Fitting 5	Fitting 6		
		$n = 10.185$	$n = 10.072$	$n = 11.486$		
		$K = 154.12$	$K = 143.31$	$K = 404.89$		
		R/nm	R/nm	R/nm	R/nm	R/nm
$RbMnF_3$	20 K	0.2111 ± 0.0004	0.2111 ± 0.0004	0.2111 ± 0.0004	0.2111 ± 0.0001[d]	0.2103 ± 0.0004
$RbMnF_3$	RT	0.2119 ± 0.0004	0.2119 ± 0.0004	0.2119 ± 0.0004	0.2120[e]	0.2122 ± 0.0004
$RbCdF_3$:Mn^{2+}	RT	0.2128 ± 0.0004	0.2128 ± 0.0004	0.2128 ± 0.0004	0.2124 ± 0.0012[f]	0.2142 ± 0.0004

a: from [1,12]; b: from [3]; c: from [3,13]; d: from [13]; e: from [3]; f: from [3,14].

Accroding to NNN model, potassium and rubidium perovskites have different n and K, and thus we must use the same optical method to calculate n and K values from fittings 1 and 4 separately. Similarly, we can derive n and K from fittings 2, 5, 3, 6, respectively. So, six sets of n, K and the corresponding R values are calculated and listed under the title NNN model in Table 3. The experimental values of R are also listed in Tables 2 and 3 for comparison. Figure 2 shows the values of R given by experiment and calculation based on NN and NNN models. The two straight lines marked as "1" and "4" in Fig.2 represent the relations $\ln 10Dq = \ln K - n\ln R$ calculated from fittings 1 and 4 by NNN model separately. The sign "Δ" stands for the calculated six values of R. The horizontal straight lines with a sign "+" represent the experimental values and errors of R. The dashed straight line marked as "7" refers to the relation $\ln 10Dq = \ln K - n\ln R$ derived by NN model. In the dashed line the six signs "×" refer to the calculated values of R. The horizontal line "8" in the center stands specifically for the value (0.2103 ± 0.0004)nm of R in $RbMnF_3$ at 20 K from NN model, and the very short horizontal line 9 refers to the corresponding experimental value $R = (0.2111 \pm 0.0001)$nm. Since in Ref.[3] there is an uncertain range of $\pm 60\,\mathrm{cm}^{-1}$ of $10Dq$ when manually choosing $10Dq$, while after using the criterion the uncertain range of $10Dq$ is only $\pm 0.1\,\mathrm{cm}^{-1}$. If we accept the errors of ± 0.0004 nm on R determined by Ref.[3], it is thus reasonable that the errors on R given by this work should be the same (± 0.0004 nm) as that in Ref.[3].

V. CONCLUSIONS

1) For any given optical spectrum, it can be forecasted that different B, C, α, and β values always lead to different $10Dq$ (see Table 2). When using NNN model six sets of different values of n and K can be derived from these values of $10Dq$ (see Table 3). However, it is surprising that after using the criterion, for every compound, different values of $10Dq$, n, and K always yield the same values of R (see Table 3). Such as in fittings 4, 5, and 6, the calculated three values of R for $RbMnF_3$ at 20 K are all equal to (0.2111 ± 0.0004)nm. which agrees well with the corresponding experimental value.

Similarly, using NN model, three sets of different values of n and K can be derived by fittings 1+4, 2+5, and 3+6 while finally three same sets of values of R are calculated (for brevity, only one set of values of R is listed, see Table 3).

The above fact shows that the criterion obviously improved the reliability of the calculated bond length through optical method. Even when we use different B, C, α, β and get different values of $10Dq$, the criterion can still lead to the same values of R. Thus the criterion solves the long existing puzzle in crystal-field theory that different parameters lead to different bond lengths. The criterion for the first time makes the bond length possible to be determined by the optical spectrum alone. It is obvious that the criterion can be widely used to any fitting of optical spectrum.

2) It can be seen from Tables 2 and 3 that although the same B, C, α, β are used in fittings 1 and 4, different NNN for potassium and rubidium systems still leads to great difference of values of n in the two systems (for potassium system, $n \simeq 5.94$; for rubidium system, $n \simeq 10.18$). On the other hand, although B, C, α, β in fittings 1, 2 and 3 are different, the same NNN (K^+) does not make the three values of n for potassium system have big differences (5.94, 5.85, 6.83). At the same time, in fittings 4, 5, and 6, different B, C, α, β and same NNN (Rb^+) make the three values of n for rubidium system close to each other (10.18, 10.07, 11.48). This fact indicates clearly that different B, C, α, β have no great influence to the exponent n while different NNN (when B, C, α, and β are the same) has obvious influence on n.

3) From Fig.2, horizontal line "8" refers to the bond length of $RbMnF_3$ at 20 K calculated with NN model, it does not agree well with the experimental value represented by very short horizontal line "9". However, after using NNN model, the six calculated values of R (designated by "Δ") agree well with the experimental values (designated by "+"). From the above it can be concluded that the NNN model is more strict and reliable.

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