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PHYSICAL REVIEW B VOLUME 3, NUMBER 3 1 FEBRUARY 1971

Vacancy-Mn^{2+} Pair Spectra in Alkali Chlorides

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(Received 27 April 1970; revised manuscript received 23 October 1970)

An attempt has been made to understand the fine-structure constants of the vacancy-associated-Mn^{2+} complexes corresponding to spectra III_1 and III_2 observed by Watkins in NaCl and KCl. The point-charge contributions arising from the mechanisms which were not considered previously are included in our treatment. The role of overlap and/or covalency effects are analyzed by calculations. Assuming the lattice distortions in accordance with the available calculations, the theoretical values of the fine-structure constants are compared with the experimental values. For spectra III_1 and III_2 the D and E values are smaller than the experimental values but they agree in sign if one considers point-charge and overlap effects. The inclusion of covalency effects brings, in general, the calculated values into better agreement with experiment. Some conclusions have also been drawn regarding the distortion of the lattice in order to improve the calculated values.

I. INTRODUCTION

Many theoretical and experimental attempts have been made in alkali halides to understand the interactions between a divalent ion impurity and a vacancy. The vacancy has been found to pair off with the divalent impurity to form vacancy-impurity pair complexes. It has been established by Watkin's electron paramagnetic resonance spectra[1] of Mn^{2+}-doped alkali chlorides that two different kinds of pair complexes can exist in such systems. One complex is formed when the vacancy is located at the cation site nearest to the magnetic ion, the spectra corresponding to which is designated by III_1. The other complex is formed when the bound vacancy is at the next-nearest cation site relative to Mn^{2+} impurity producing spectra III_2. These spectra have been interpreted by Watkins by means of the theory then available which considered the contributions from the spin-spin mechanism arising from $d \rightarrow s$ excitation only and the Watanabe mechanism. The theory was found to give the correct sign but the results were an order of magnitude too low. No attempt has yet been made in such systems to estimate the contributions from overlap and/or charge transfer effects, though the importance of these has been emphasized by Watkins. Since now other mechanisms are known to give dominant contributions, it is of interest to know whether the conclusions of Watkins change if one incorporates the effects of these mechanisms. This has been done in the present paper. Moreover, the contributions from overlap effects have also been calculated. The spectra we have considered in the present paper are III_1 and III_2 in NaCl and KCl crystals.

In Sec. II we present the procedure and the calculations for the ground-state splittings of the complexes III_1 and III_2 in NaCl and KCl and compare them with the experimental results. The discussion is given in Sec. III, where some speculations have also been made to bring the theoretical results into line with experiment.

II. PROCEDURE AND RESULTS

The expressions derived in Refs. 2 and 3 may be used here directly with appropriate changes to estimate the ground-state splitting parameters D and E for spectra III_1 and III_2. In the following, we first consider spectra III_1 and obtain point-charge contributions from various mechanisms[2] — Blume-Orbach (BO), spin-spin (SS) ($d \rightarrow s$, $d \rightarrow d$, $d \rightarrow g$), Watanabe-with-cubic field (WC), and Orbach-Das-Sharma (ODS) mechanisms — and overlap contributions in NaCl and KCl. Next we consider spectra III_2 and give similar results.

A. Spectra III_1

The vacancy-Mn^{2+} pair complex which gives rise to the spectra III_1 is shown in Fig. 1. Bassini and Fumi[4] have estimated the displacements of the ions for this complex in NaCl and KCl with the impurity ions Cd^{2+}, Ca^{2+}, and Sr^{2+}. To the knowledge of the authors, no similar calculations have yet been reported for the case where the impurity ion is Mn^{2+}. In the absence of such data, we assume that the displacements of the ions when Mn^{2+} is present as

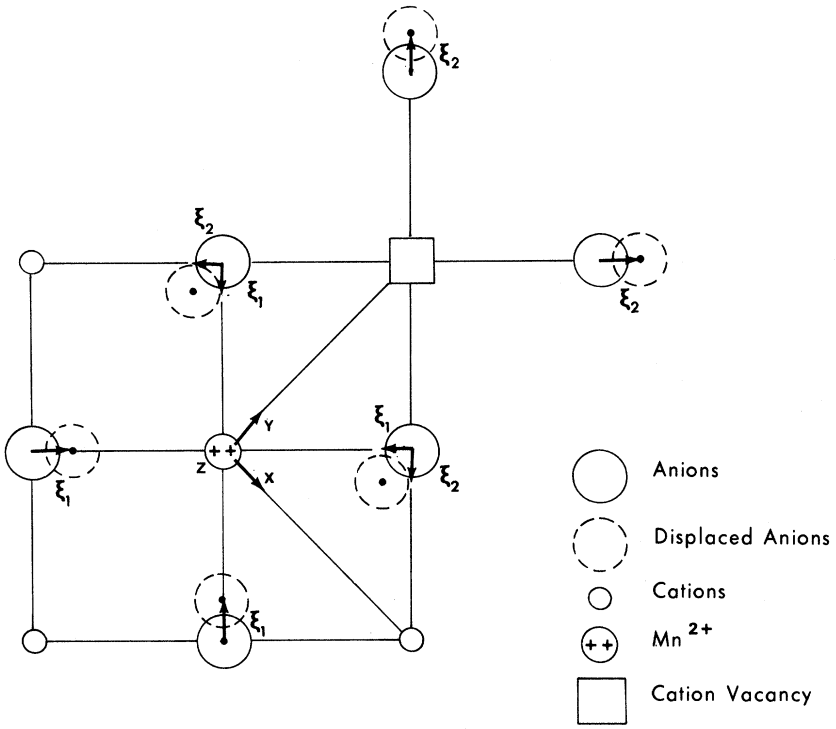

FIG. 1. Vacancy-Mn^{2+} pair complex corresponding to spectra III_1.

an impurity are not drastically different from those estimated by Bassani and Fumi. In Fig. 1, $\xi_1 a$ designates the displacements of the anions nearest to the impurity, and $\xi_2 a$ the displacements of the anions nearest to the vacancy, a being the nearest-neighbor distance. If we suppose that the crystal fields at the Mn^{2+} site arise from the point charges alone, then we have, to the first order in the displacements,

$$B_2^0 = (1/a^3)\{(1/2\sqrt{2}) - [(12/25\sqrt{5}) + (8/9\sqrt{3})]\xi_2\},$$

$$B_4^0 = (1/4a^5)\{-(3/4\sqrt{2}) + 100\xi_1 + [(12/25\sqrt{5}) - (40/81\sqrt{3})]\xi_2\},$$

$$B_4^4 = (\sqrt{70}/8a^5)\{-(1/4\sqrt{2}) + 20\xi_1 + [(332/3125\sqrt{5}) + (8/27\sqrt{3})]\xi_2\},$$

$$(B_4^0)' = B_4^0 + (14/5)^{1/2} B_4^4,$$

$$B_2^2 = ((3/2)^{1/2}/a^3)\{(1/2\sqrt{2}) - [4 + (12/25\sqrt{5}) + (20/27\sqrt{3})]\xi_2\},$$

$$B_4^2 = (\sqrt{10}/2a^5)\{(-1/4\sqrt{2}) + 2[2 + (46/625\sqrt{5})]\xi_2\},$$

where the crystal fields given above are defined in Ref. 2; the B_2^0 and B_2^2 are in units of $e^2/2a_0^3$, whereas B_4^0, B_4^4, $(B_4^0)'$, and B_4^2 are in units of $e^2/2a_0^5$; a (the nearest-neighbor distance) is in units of a_0.

It is interesting to mention that the crystal fields B_2^0, $(B_4^0)'$, B_2^2, and B_4^2 are independent of the parameter ξ_1 which must be the case since such displacements of the nearest neighbors produce cubic symmetry at the impurity site. The $(14/5)^{1/2}$ in the expression for $(B_4^0)'$ has been obtained in the same manner as described previously.[2,5]

For the calculations of the crystal fields we select the values of the parameters ξ_1 and ξ_2 appropriate to the Sr^{2+} impurity because the displacements for spectra III_2 are available only for Sr^{2+} impurity[6] and it is more meaningful to compare the results (for spectra III_1 and III_2) if they are calculated on the same basis. The crystal fields are then used to estimate the splitting parameters D and E for spectra III_1. The combined results from various mechanisms are tabulated in Table I for NaCl and KCl. The comparison of the result for D (spectra III_1, NaCl) with the corresponding experimental value (Table II) shows that they agree in sign, but the calculated result is about a factor of 7 too low. The D value estimated by Watkins corresponds to the contributions from the SS($d \rightarrow s$) mechanism (the Watanabe contribution being neglected, since it is an order of magnitude lower), i. e., -1.02 (in units of 10^{-4} cm^{-1}). This value agrees in sign but is about 45 times smaller than the experimental result. This was essentially the conclusion arrived at by Watkins. Thus, it is easy to see that the consideration of the other mechanisms (especially the BO mechanism) has changed Watkin's calculated results very significantly beyond the value from the SS ($d \rightarrow s$) mechanism. The situation for D in KCl is similar to this (see Tables I and II). However, one point is noteworthy: The total D value is lower

TABLE I. Point-charge and overlap contributions (in units of 10^{-4} cm^{-1}) to the ground-state splitting parameters D and E for spectra III_1 and III_2 in NaCl and KCl.

	Point-charge contribution			Overlap contribution		
Spectra	III_1		III_2	III_1		III_2
Parameter						
Crystal	D	E	D	D	E	D
NaCl	−5.61	−9.57	−3.00	+0.38	+11.78	+6.67
KCl	−3.46	−5.28	−1.68	+0.99	+ 8.33	+6.74

in KCl than in NaCl since the nearest-neighbor distance is larger in KCl than in NaCl, while ξ_2 stays almost the same (0.081 in KCl and 0.083 in NaCl), consequently decreasing the crystal fields in KCl.

As for the parameter E, we mention that its sign is not known from the experiment[7] since it was not possible to distinguish whether the vacancy was along the x or y axis. If one believes that the vacancy lies on the y axis, one gets a disagreement in sign in this case. The magnitudes of E are smaller by a factor of 4 in NaCl and 8 in KCl compared with the experimental values. The contributions from the SS($d \rightarrow s$) mechanism are $+0.17\times10^{-4}$ cm^{-1} in NaCl and $+0.08\times10^{-4}$ cm^{-1} in KCl. The BO contributions (-9.82×10^{-4} cm^{-1} in NaCl and -5.40×10^{-4} cm^{-1} in KCl) completely change the sign and magnitude of the total contribution to E in both NaCl and KCl. The parameter E was not estimated by Watkins for our comparison, probably because the relevant expressions for E were not known.

To estimate the effects of overlap, one needs to find expressions for D and E for spectra III_1 similar to those given in Ref. 3. The nearest neighbors of the magnetic ion in the case of spectra III_1 are differently located than in Ref. 3 (compare Fig. 1 here and Fig. 1 of Ref. 3). A detailed investigation shows that the expressions for D and E in Ref. 3 should be divided by a factor of 2 so that they are applicable for spectra III_1. This is physically clear if one remembers that D is nonzero when the distance from Mn^{2+} of the two neighboring ions on the z axis is different than that of the four ions on the plane perpendicular to the axis. In spectra III_1, only two of the four neighboring ions on the plane have a different distance from the Mn^{2+} (relative to those on the z axis) and hence the contribution to D in this case is half of that in Ref. 3. The parameter E, on the other hand, is nonzero when the four ions on the plane do not form a perfect square. In the present case, only two of the four ions contribute to the deformation of the square, which explains the factor of 2 in case of E.

The various overlap integrals[8] useful for SS and spin-orbit interactions are calculated for NaCl and KCl using a general expression for the α function.[9] For the calculation of these integrals, we have used Watson's wave function[10] for the $3d$ electrons of Mn^{2+} and Clementi's wave functions[11] for the $3s$ and $3p$ electrons of chlorine ions, and followed the procedure given in Ref. 3. The other parameter is ζ_{pp} (Cl^-), the spin-orbit coupling constant for $3p$ electrons of Cl^-, which is calculated to be 242 cm^{-1}. The overlap contributions to D and E are listed in Table I for both NaCl and KCl.

Comparison of Tables I and II shows that the overlap effects are able to explain the spectra III_1 (especially E) in NaCl and KCl. The signs of the overlap D values are not the same as the experimental values, and they are very low, even lower than the point-charge contributions. The calculated overlap E values are of correct sign[7] but are low in both NaCl and KCl.

B. Spectra III_2

The vacancy-Mn^{2+} pair complex associated with spectra III_2 is depicted in Fig. 2. The displacements of the surrounding ions, shown in the figure, are in accordance with the calculations of a similar pair by Tosi and Airoldi[6] where a Sr^{2+} next-nearest cation vacancy complex has been considered. The displacement of the anion between the impurity and the vacancy is taken to be ηa. The other ions nearest to the impurity are displaced by $\xi_1 a$ towards the impurity site, and the remaining ions nearest to the vacancy by $\xi_2 a$ away from the vacancy. The crystal fields at the Mn^{2+} ion required in this case are

$$B_2^0 = (1/a^3)\{-1/4 - 6(\eta - \xi_1) + [\tfrac{2}{27} + (36/25\sqrt{5})]\xi_2\},$$

$$(B_4^0)' = (1/a^5)\{-1/16 + 10(\eta - \xi_1) + [\tfrac{10}{279} + (243/625\sqrt{5}) + (77/3125\sqrt{5})]\xi_2\},$$

where again B_2^0 is in units of $e^2/2a_0^3$, and $(B_4^0)'$ is in units of $e^2/2a_0^5$; a is in units of a_0. Because of the symmetry, the crystal fields which contribute to E are absent in this case.

Using the parameters ξ_1, ξ_2, and η given in Ref. 6, we now calculate B_2^0 and $(B_4^0)'$ and hence the splitting parameters D which are listed in Table I for both NaCl and KCl. These values are of the wrong sign and an order of magnitude smaller than the corresponding experimental values (see Table II).

TABLE II. Experimental values (in units of 10^{-4} cm^{-1}) of D and E as determined by Watkins.

Spectra	III_1		III_2
Parameter	D	E	D
Crystal			
NaCl	−45.0	40.7	43.67
KCl	−66.0	41.0	58.0

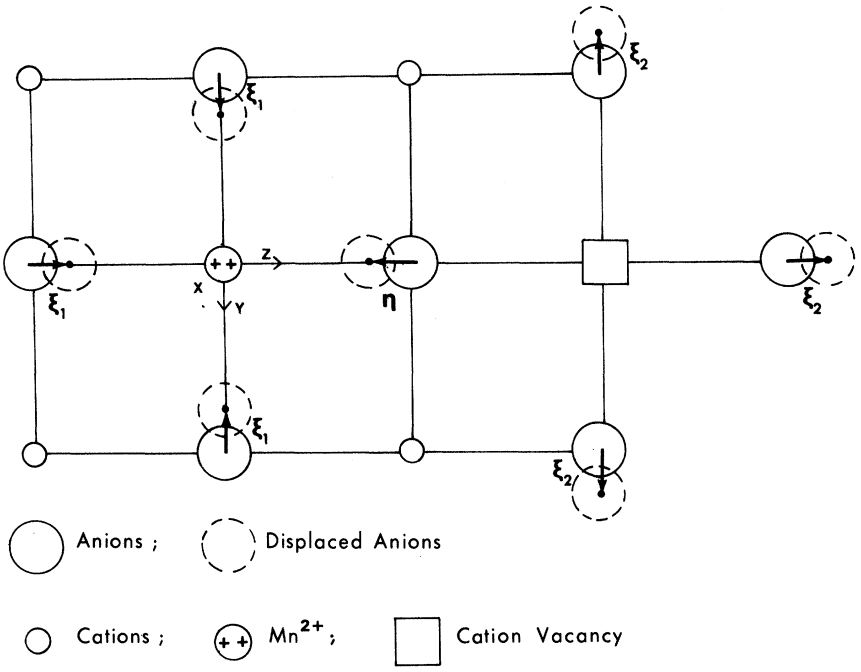

FIG. 2. Vacancy-Mn^{2+} pair complex corresponding to spectra III_2.

We next consider overlap effects in this case. Since only one of the two ions nearest to Mn^{2+} on the z axis is differently spaced than the nearest ions on the plane perpendicular to the z axis, one must divide the expressions of Ref. 3 by a factor of 2. The various overlap integrals[8] for KCl and NaCl are again estimated using the general expression for the α function[9] as explained in Ref. 3. From these, one may now estimate the D values which are shown in Table I. The overlap D values are of the correct sign and about six and eight times smaller than the experimental values for NaCl and KCl, respectively.

III. DISCUSSION

Using the appropriate lattice distortion parameters as calculated in Refs. 4 and 6, we have analyzed the fine-structure parameters D and E for spectra III_1 and III_2 in NaCl and KCl, both from the point-charge and overlap models. The total values for the spectra in NaCl and KCl agree in sign but are about an order of magnitude too small. Thus, if we wish to get a good agreement with the experiment, we should increase the magnitudes of D and E. There are two effects which we have not yet included in our treatment. One is the effect of the induced dipoles on the lattice and the other, the effect of the charge transfer covalency. In the following, we explain how our results are changed by these effects.

The effect of the induced dipoles can be incorporated into the crystal fields simply by increasing or decreasing slightly the values of the displacement dipoles ξ_1, ξ_2, and η. Since the values of the induced dipoles are not known in our cases, it is difficult to assess directly the importance of this effect. Thus, it is appropriate to investigate the possibility of improving our results by changing slightly the values of the displacement parameters. First, let us consider spectra III_1. In the point-charge model the BO contributions are dominant and, therefore, to change the magnitudes of D and E, the crystal fields $(B_4^0)'$ and B_4^2 should be changed. This can be affected by changing the value of ξ_2. It can be seen that D is insensitive to changes in ξ_2, while E can be decreased if ξ_2 is decreased. As for the overlap contributions, the nonlocal spin-spin and local spin-orbit contributions are dominant. The D parameter can be improved by decreasing ξ_2, since D is approximately proportional to the difference of the squares of the overlaps of the magnetic ion with the two Cl^- ions, one located on the z axis and the other on the plane perpendicular to this axis. Such a decrease in ξ_2 will, however, not improve E, since E depends on the cosine of the angle between the lines joining the magnetic site to the two Cl^- sites on the plane perpendicular to the z axis.[3] A more important point, however, is that the charge-charge transfer covalency improves E but not D. If the covalency parameters are close to the corresponding overlap parameters,[12] E can be improved by almost a factor of 2, thereby bringing E close to the experiment.

We now analyze critically the parameter D in spectra III_2. If the displacement ξ_2 is varied to improve the point-charge results, one observes that one cannot reverse the sign of D (even by changing the sign

of ξ_2). The increase in magnitude of η also does not improve the results. For instance, if η is doubled, the SS contribution changes from $+2.31 \times 10^{-4}\,\mathrm{cm}^{-1}$ to $+4\times10^{-4}\,\mathrm{cm}^{-1}$ and the BO contribution further increases in magnitude from its value $-5.34 \times 10^{-4}\,\mathrm{cm}^{-1}$ without changing the sign of the combined result. However, improvement can be obtained by decreasing the magnitude of η or preferably changing its sign. Keeping the same order of magnitude,[13] but taking the opposite sign of η makes the SS and BO contributions, respectively, -2 and $+5$ (in units of $10^{-4}\,\mathrm{cm}^{-1}$), which give a net positive value to D.

On the other hand, it can be seen that by increasing η one can improve the overlap contributions. The introduction of covalency parameters[14] (if they lie close to the corresponding overlap parameters) can further improve the results by almost a factor of 2.

Thus, a reasonable agreement can be obtained if one changes the magnitude of ξ_2 in spectra III_1 and changes the sign of η in spectra III_2. The change in the value of ξ_2 in III_1 is expected if one considers, on physical grounds, the effect of induced dipoles. Moreover, we have taken the distortion parameters appropriate to Sr^{2+}-vacancy complexes which may be quite different in our case. Regarding the change in η, it has been argued by Tosi and Airoldi[15] that the parameter η may suffer a large error because of the uncertainties of the repulsive interaction at short distances.

There is one more important point which must be mentioned. It is regarding the off-center displacement of the impurity ion. This possibility has not been considered in Refs. 4 and 6 for the calculations of the distortion parameters. Since the considerable difference[4] between the association energies for Cd^{2+} and Ca^{2+} in NaCl has not been explained, it is important to investigate such a displacement and its influence on the other distortion parameters. The displacement of the impurity ion (especially for spectra III_1) towards the vacancy is expected because the impurity ion is a positive center and the vacancy is effectively a negative center. This displacement is consistent with the experiment[1] where D and E are nonzero for spectra III_1 and E is zero for III_2. Our results change only slightly if the displacement of the magnetic ion is taken into account. The maximum changes in fine-structure constants are 0.3 and 3 (in units of $10^{-4}\,\mathrm{cm}^{-1}$) if the displacement is $0.01a$ and $0.1a$, respectively. Though this change is small in our case, it may be important for the calculations in Refs. 4 and 6 to improve the association energies and may indirectly affect the values of the parameters ξ_2 and η which are useful for our calculations.

Therefore, in order to explain quantitatively the observed fine-structure constants, a first-principles calculation[16] of the distortion parameters is really needed for vacancy-associated Mn^{2+} complexes — one in which the magnetic ion is allowed to shift from the lattice site.

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[7]See footnote 29 of Ref. 1.

[8]The tables of these integrals are available on request from the authors.

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[10]R. E. Watson, MIT Solid State Molecular Group Technical Report No. 12, 1959 (unpublished).

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[12]Though there is no reason why the covalency parameters should be close to the corresponding overlap parameters, we have assumed this to show that E improves by taking covalency into account.

[13]It is difficult to justify why the magnitude of η should be the same when its sign changes. However, this has been assumed here simply to demonstrate that, as η decreases and finally changes sign and increases in magnitude, the point-charge D value comes closer to the experiment.

[14]One could very well consider the effect of covalency before speculating on the parameter η.

[15]See p. 587 of Ref. 6.

[16]The calculation should include the overlap and charge transfer covalency effects in minimizing the energy, in order to extract information about the covalency parameters.