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Calculation of the shape of the potential well of Mn^{2+} in $SrCl_2$

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The shape of the potential energy well of Mn^{2+} as an impurity in $SrCl_2$ has been calculated, using the method of Wilson *et al.* for a polarizable-point-ion model. For these calculations the parameters of the Born repulsion potential $B \exp(-r/\rho)$ have been derived for the Sr-Cl and Mn-Cl interaction. It has been shown that the potential energy varies less than 0.01 eV over distances of 0.3, 0.5, and 0.4 Å along $\langle 100 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$, respectively. This result is in agreement with experiment.

I. INTRODUCTION

Recent experiments on the electric-field effect in EPR of $SrCl_2 : Mn^{2+}$ have shown that the shape of the potential well, that is seen by the Mn^{2+} ion, is very flat.[1] $SrCl_2$ has the well-known fluorite structure, which consists of three interpenetrating fcc lattices; the Sr ions are at (0, 0, 0), the Cl(1) at (0.25, 0.25, 0.25), and Cl(2) at (0.75, 0.75, 0.75). A simple one-dimensional model reveals that for displacements of the impurity along the $\langle 111 \rangle$ direction the potential-energy curve should have the form indicated in Fig. 1. The system can be described as an intermediate system between an off-center and a normal substitutional system. In this case there is a cancellation of mainly repulsive and polarization forces over a distance of about 0.5 Å. The methods that have been developed for the calculation of the form of the potential well of off-center systems, can also be applied to the $SrCl_2 : Mn^{2+}$ system. In this paper we present results of such calculations; our principal aim has been to find a theoretical confirmation that the potential energy curve for displacements of the impurity along the $\langle 111 \rangle$ is flat within 0.01 eV over a distance of about 0.5 Å.

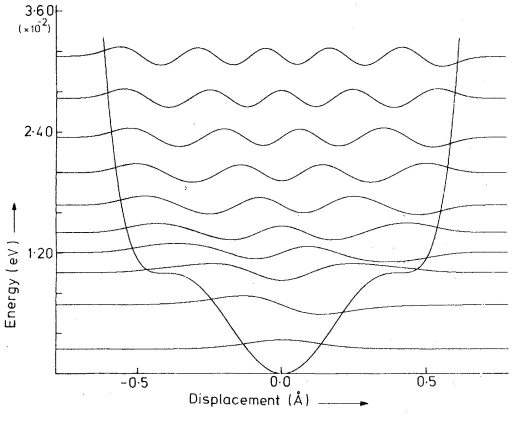

FIG. 1. Approximate form of the potential well, seen by the Mn^{2+} ion for displacements along the $\langle 111 \rangle$ direction. This shape of the well is based on experimental results of the electric field effect in EPR of $SrCl_2$: Mn^{2+} (Ref. 1). The wave functions and energy levels have been indicated.

II. METHOD OF CALCULATION

We use the polarizable-point-ion (PPI) model in order to describe the interactions between the ions. The use of the PPI model is justified, because the binding in $SrCl_2$ is known to be almost fully ionic. The method for the calculation of the form of the potential well is described elsewhere,[2] and is a slight variation of the one used by Wilson *et al.*[3] for the calculations on $KCl : Li^+$. The reader is referred to Ref. 2 for the expressions that give the various contributions to the potential energy. Because we are dealing with a different crystal structure, the Taylor-series expansion of the electrostatic potential of the unperturbed lattice for a displacement of the impurity from its lattice site $\vec{r}$ to the actual position $\vec{r}'$ now reads

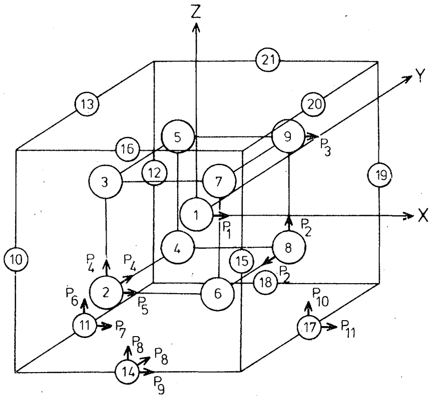

FIG. 2. Schematic representation of displacement parameters for a displacement of the impurity along the $\langle 100 \rangle$ directions. The parameters have been indicated only for one of each group of ions, which are equivalent by C_{4v} symmetry.

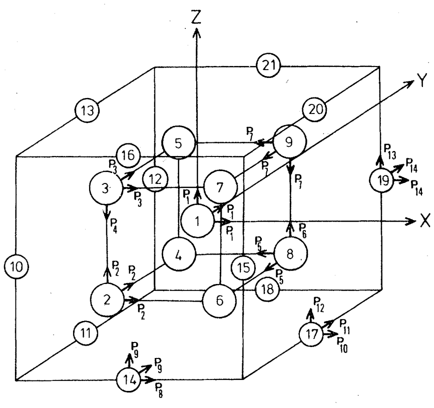

FIG. 3. Schematic representation of displacement parameters for a displacement of the impurity along the ⟨111⟩ directions. The parameters have been indicated only for one of each group of ions, which are equivalent by C_{3v} symmetry.

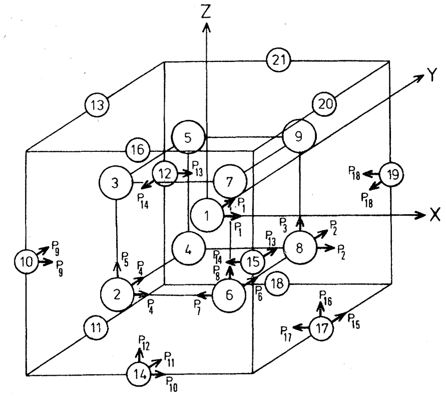

FIG. 4. Schematic representation of displacement parameters for a displacement of the impurity along the ⟨110⟩ directions. The parameters have been indicated only for one of each group of ions, which are equivalent by C_{2v} symmetry.

$$V(\vec{x}) = \frac{e}{a}[183.8186(x_1^4+x_2^4+x_3^4) - 551.4558(x_1^2x_2^2+x_2^2x_3^2+x_3^2x_1^2) - 677.0429(x_1^6+x_2^6+x_3^6) - 60933.8600x_1^2x_2^2x_3^2 + 5077.8217(x_1^4x_2^2+x_2^4x_3^2+x_3^4x_1^2+x_1^4x_3^2+x_2^4x_1^2+x_3^4x_2^2)], \tag{1}$$

for the Sr^{2+} site, where a is the lattice constant, $\vec{r}' - \vec{r} = a\vec{x}$, and e is the elementary charge. For a Cl(1) ion we have

$$V(\vec{x}) = \frac{e}{a}[614.4907x_1x_2x_3 - 298.3332(x_1^4+x_2^4+x_3^4) + 894.9997(x_1^2x_2^2+x_2^2x_3^2+x_3^2x_1^2) + 550.3870(x_1^6+x_2^6+x_3^6) + 49534.8257x_1^2x_2^2x_3^2 - 4127.9021(x_1^4x_2^2+x_2^4x_3^2+x_3^4x_1^2+x_1^4x_3^2+x_2^4x_1^2+x_3^4x_2^2)]. \tag{2}$$

For a Cl(2) ion the coefficient of $x_1x_2x_3$ has to be −614.4907.

The calculations were carried out for displacement of the Mn^{2+} ion along the ⟨100⟩, ⟨111⟩, and ⟨110⟩ directions. The relaxation of the ions is described in these cases by the displacement parameters, which are represented schematically in Figs. 2–4.

III. DETERMINATION OF PPI MODEL PARAMETERS

A. Polarizabilities

The polarizabilities of Sr^{2+} and Cl^- were taken from the work of Tessman *et al.*[4] For $\alpha_{Mn^{2+}}$ we used the value, obtained in Ref. 2.

B. Short-range interactions

As compared to the alkali halides, little systematic work has been done (except for the fluorides [see, e.g., Ref. 5]) on the alkaline-earth halides, and nothing is known about the short-range potential for the Mn-Cl interaction. Therefore we have to resort to *ad hoc* methods for a first approximation of the short-range potentials.

1. Short-range interaction of Sr-Cl and Cl-Cl

Following the line of reasoning used for the alkali halides, we try to determine the short-range potential from the elastic constants of $SrCl_2$. If we assume, that there is only short-range interaction between Sr-Cl and nearest neighbors Cl(1)-Cl(2), there are four force constants that have to be determined. In a crystal with cubic symmetry, there are three elastic constants. However, the electronic polarizability of the ions appears in the expression for C_{44}. Because of this, the determination of the force constants is not as straightforward as for the alkali halides. Kühner *et al.*[6] have determined force constants for the Axe shell model.[7] The values are A(Sr-Cl) = 33.600; B(Sr-Cl) = −2.5074; A[Cl(1)-Cl(2)] = 4.2452; B[Cl(1)-Cl(2)] = 0.09484, where

TABLE I. Input data.

Lattice constant: 6.984 Å

$r_{\min}$ (Mn-Cl) = 2.47 Å; $r_{\min}$ (Sr-Cl) = 2.87 Å; $r_{\min}$ (Cl-Cl) = 3.32/3.14 Å

Repulsion parameters

	B (erg)			ρ (Å)			Polarizabilities (Å$_3$)
	Mn	Sr	Cl	Mn	Sr	Cl	
Mn	0	0	1.4734×10^{-8}	⋯	⋯	0.2264	0.912
Sr	0	0	3.0570×10^{-7}	⋯	⋯	0.2257	1.55
Cl	1.4734×10^{-8}	3.0570×10^{-7}	1.9661×10^{-9}	0.2664	0.2257	0.3214	2.974

$$\frac{1}{r_0'}\frac{d\phi^{\mathrm{SR}}}{dr}\bigg|_{r_0'} = B\left(\frac{e^2}{v_0}\right), \tag{3}$$

$$\frac{d^2\phi^{\mathrm{SR}}}{dr^2}\bigg|_{r_0'} = A\left(\frac{e^2}{v_0}\right), \tag{4}$$

$$r_0' = \tfrac{1}{2}r_0\sqrt{3}\ , \tag{5}$$

$$v_0 = 2r_0^3\ , \tag{6}$$

where r_0 is the nearest-neighbor Cl(1)-Cl(2) distance = 3.492 Å. For the Sr-Cl interaction, we can evaluate the parameters B and ρ of a Born repulsive potential

$$\phi_{\mathrm{Sr,Cl}}(r) = B\exp(-r/\rho)\ . \tag{7}$$

The results are given in Table I. For the Cl(1)-Cl(2) interaction, we note that B and A are both positive so that at this distance the short-range part of the Cl(1)-Cl(2) potential is attractive. This means, that the van der Waals term is of the same order of magnitude as the repulsion terms; it is not possible in this way to evaluate the form of the short-range interaction from the force constants. Recently, Catlow et al.[8] have determined two sets of short-range potentials for the alkali halides. There are some difficulties with their potentials, especially for interionic distances smaller than ~3.5 Å, because of the unavailability of experimental data in the alkali halides in this region. For our calculations this region is of special importance. The equilibrium distance of nearest-neighbor chlorine ions in $SrCl_2$ is 3.49 Å, and consequently one needs the short-range potential for distances between about 3.1 and 4.0 Å. According to the second potential, the equilibrium distance of 3.49 Å lies in the repulsive region. The Axe shell model, however, yields an attractive interaction. Because of these uncertainties, we have taken the more simple potential from the first set for the Cl-Cl interaction in LiCl. The equilibrium distance of the chlorine ions in LiCl is approximately the same as in $SrCl_2$.

2. *Mn-Cl repulsion*

We now turn our attention to the problem of finding the Mn-Cl repulsion. We have determined the Mn-Cl repulsion from the Raman frequencies of $MnCl_2$. $MnCl_2$ has the trigonal $CdCl_2$ structure.[9] Its space group is D_{3d}^5. The crystal is composed of layers; each layer consists of three planes, one of Mn ions surrounded on either side by a plane of chlorine ions. The hexagonal unit cell contains three of these layers. If we put the Mn ions in the (0, 0, 0) position, then the chlorine ions are in the $(0, 0, \pm h)$ positions. For all the crystals in the $CdCl_2$ family h is between 0.25 and 0.26.[9] For $MnCl_2$ the value of h is not known. We assume that it is 0.25.

Ghosh[10] has successfully explained the frequencies of the infrared and Raman modes by assuming that there are only binding forces inside the layers. It is assumed that the layers are held together by van der Waals forces, which are about 100 times as weak as the intralayer forces. In the following we shall derive the form of the repulsion potential for the Mn-Cl interaction, adopting the PPI model. Whether this is justified, will become evident from the results of this calculation, and ultimately from the results of the $SrCl_2 : Mn^{2+}$ calculations.

We shall assume that we have rigid planes, so the positions of the ions in the planes are fixed. Further we shall assume, that there are only intralayer forces. The vibrational modes of the planes in one layer are given schematically in Fig. 5.

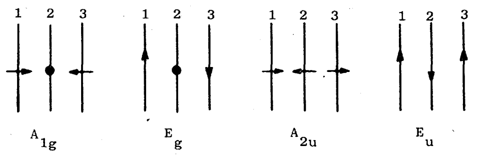

FIG. 5. Vibrational modes of $MnCl_2$.

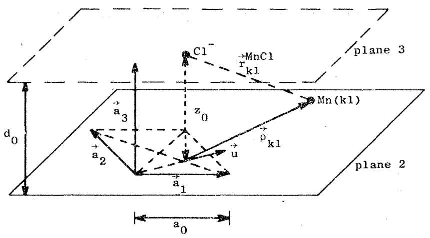

FIG. 6. Sketch of two planes in $MnCl_2$ with relevant quantities (see text).

The A_{1g} and E_g mode are Raman active and the A_{2u} and E_u mode are infrared active. We shall use the experimental values of the Raman frequencies, because then the polarizability of Mn^{2+} is not involved. Denoting the distance from plane 1 to 2, and of plane 2 to 3 by d, and the displacement of plane 3 relative to plane 2 along the plane 3, by u (Fig. 6), the potential energy of a layer is a function of d and u. We have the equilibrium condition

$$\left.\frac{dV(d,u)}{dd}\right|_{d=d_0,\, u=0} = 0. \tag{8}$$

Because of symmetry,

$$\left.\frac{dV(d,u)}{du}\right|_{d=d_0,\, u=0} = 0. \tag{9}$$

From the equations of motion, we have

$$2m\omega^2(A_{1g}) = \left.\frac{d^2V}{dd^2}\right|_{d=d_0,\, u=0} \tag{10}$$

and

$$2m\omega^2(E_g) = \left.\frac{d^2V}{du^2}\right|_{d=d_0,\, u=0} . \tag{11}$$

Consequently, we have to derive an expression for $V(d,u)$. We split V into

$$V(d,u) = V_C(d,u) + V_{SR}(d,u) . \tag{12}$$

V_C is the Coulomb part, and V_{SR} is the short-range part of the total potential energy. V_C can be written

$$V_C = Z_3 e\phi_1(d,u) + 2Z_3 e\phi_2(d,u) - 2\times\tfrac{1}{2}\alpha E_t^2 . \tag{13}$$

Here Z_3 is the charge of the ions in plane 3, ϕ_1 the Coulomb potential of plane 1 at plane 3, ϕ_2 the Coulomb potential of plane 2 at plane 3, and E_t the total electric field at plane 3. Setting up a coordinate system with axes $\vec{a}_1$ $(=a_0\vec{e}_1)$, $\vec{a}_2$ $(=a_0\vec{e}_2)$ and

$$\vec{a}_3 = \frac{d_0(\vec{a}_1\times\vec{a}_2)}{|\vec{a}_1\times\vec{a}_2|}\ (=d_0\vec{e}_3) , \tag{14}$$

(Fig. 6) we can show that

$$\phi_1(d,u) = Z_1 e \sum_{kl} \frac{1}{|\vec{r}_{kl}^{\,\mathrm{Cl\,Cl}}|} , \tag{15a}$$

where

$$\vec{r}_{kl}^{\,\mathrm{Cl\,Cl}} = \left[(k - \tfrac{1}{2}l - 1 - \delta\sqrt{3})\vec{e}_1 + (\tfrac{1}{2}l\sqrt{3} - \tfrac{1}{3}\sqrt{3} - \delta)\vec{e}_2 - 2\gamma\vec{e}_3 \right] a_0 \tag{15b}$$

and

$$\phi_2(d,u) = Z_2 e \sum_{kl} \frac{1}{|\vec{r}_{kl}^{\,\mathrm{MnCl}}|} , \tag{16a}$$

where

$$\vec{r}_{kl}^{\,\mathrm{MnCl}} = \left[(k - \tfrac{1}{2}l - \tfrac{1}{2} - \tfrac{1}{2}\delta\sqrt{3})\vec{e}_1 + (\tfrac{1}{2}l\sqrt{3} - \tfrac{1}{6}\sqrt{3} - \tfrac{1}{2}\delta)\vec{e}_2 - \gamma\vec{e}_3 \right] a_0 , \tag{16b}$$

and

$$d = \gamma a_0 \tag{17}$$

and

$$u = \delta a_0 . \tag{18}$$

E_t can be written

$$E_t = E_C + E_{\mathrm{dip}} , \tag{19}$$

where

$$E_C = -\frac{d\phi_1}{dz} - \frac{d\phi_2}{dz} . \tag{20}$$

The positions of the ions in plane 3 relative to one particular Cl^- ion are given by

$$\vec{S}_{kl} = (k\vec{e}_1 + l\vec{e}_2)a_0 . \tag{21}$$

It is very easy to see, that in equilibrium there will be static dipolar moments on the Cl^- ions, which are perpendicular to the planes. If we neglect dipolar moments, directed along the planes, and the field of the dipoles of plane 1 at plane 3, upon displacement of the planes from their equilibrium, we can write

$$E_{\mathrm{dip}} = -\sum_{\substack{kl \\ |S_{kl}| \neq 0}} \frac{P}{|\vec{S}_{kl}|^3} , \tag{22}$$

where

$$p = \alpha E_t . \tag{23}$$

From (19), (22), and (23) now follows

$$E_t = E_c / C_{\mathrm{pol}} , \tag{24}$$

with

$$C_{\mathrm{pol}} = (1 + \alpha \sum_{\substack{kl \\ |S_{kl}| \neq 0}} |S_{kl}|^{-3}) . \tag{25}$$

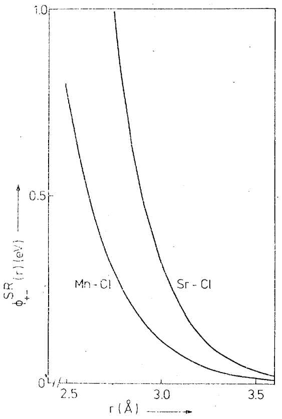

FIG. 7. Graphs of repulsion potentials of Mn-Cl and Sr-Cl interaction.

For the short-range part of the potential energy in (12) we can write

$$V_{SR}(d)=6\phi_{+-}(r(d)), \tag{26}$$

where

$$r(d)=(\tfrac{1}{3}a_0^2+d^2)^{1/2}. \tag{27}$$

Now we have expressions for $V(d,u)$, from which follow after some algebra the expressions for the derivatives of $V(d,u)$. a_0 has the value 3.7061 Å,[11] and from the value of c_0 we calculate $d_0=1.464$ Å. From the equilibrium condition (8) we obtain

$$\phi'_{+-}(r(d_0))=-3.282\times10^{-4}\,\text{dyn}.$$

As quoted in Ref. 10, $\omega(A_{1g})=234.5$ cm^{-1}. By (10), we have $\phi''(r(d_0))=-6.5\times10^4$ dyn/cm. Evidently, this is the wrong sign. So we have neglected something in our model, or we have used inaccurate input data, such as the value of h. We note that the equilibrium Mn-Cl distance is about 2.6 Å, whereas the distance of planes 1 and 2 is about 1.4 Å. This means that the angle between the line connecting the Mn and Cl ions, and the normal to the plane is ≈60°, which enhances the error in the value of h. We expect that E_g motion suffers less from this effect. As quoted in Ref. 10, $\omega(E_g)=144$ cm^{-1}. From (8) and (11) we determine ϕ'' as

$$\phi''(r(d_0))=1.232\times10^5\,\text{dyn/cm}.$$

Assuming a Born repulsive potential, we have

$$\phi(r)=1.4734\times10^{-8}\exp-r/0.2664\ (\text{erg}). \tag{28}$$

These values are of the right order of magnitude. The potentials for the short-range interaction between Sr-Cl and Mn-Cl are displayed in Fig. 7. We observe that the Mn-Cl potential indeed yields a repulsion weaker than the Sr-Cl potential for distances smaller than ≈3 Å, which is the equilibrium distance in $SrCl_2$.

In order to prevent a "polarization catastrophe," a defect of the PPI model in some of the calculations on the alkali halides[3,2] a term

$$\phi(r)=100\,000[1-(r/r_{min})]\,\text{eV},$$

is added to the repulsion potential for r smaller than an adjustable distance r_{min}.

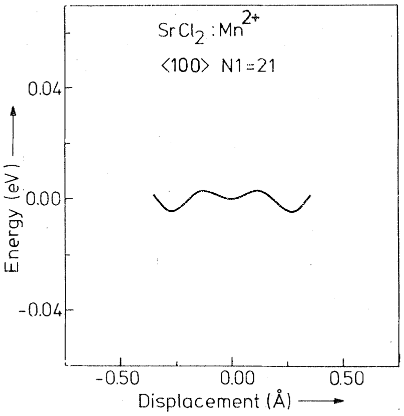

FIG. 8. Calculated potential energy of Mn^{2+} in $SrCl_2$ as a function of the displacement of the impurity along the ⟨100⟩ directions, with $r_{min}=3.32$ Å.

IV. CALCULATIONS

The input data for $SrCl_2$: Mn^{2+} are summarized in Table I. The results are given in Figs. 8–13. We added a term $0.34/r^6$(eV) to the Born repulsion potential for Cl-Cl interaction (in accordance with Sec. III B 1) if the distance between the chlorine ions was greater than r_{min}. The number of relaxing ions was 21. For the number of ions in region I+II,[3] we have taken 131. For this number, the total charge of the ions surrounding the impurity is $-4e$. For a number of 421 ions this charge is zero. But this implies a lengthening of com-

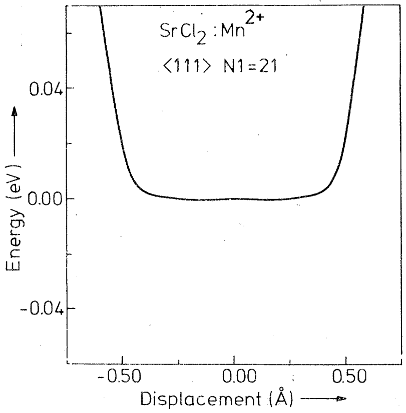

FIG. 9. Calculated potential energy of Mn^{2+} in $SrCl_2$ as a function of the displacement of the impurity along the ⟨111⟩ directions, with $r_{min}=3.32$ Å.

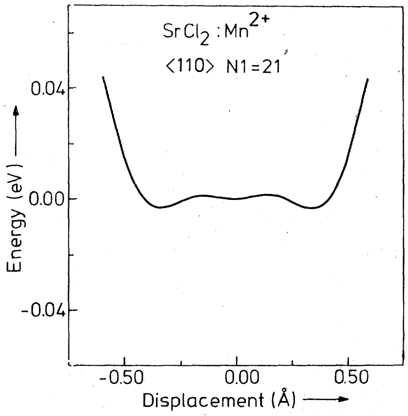

FIG. 10. Calculated potential energy of Mn^{2+} in $SrCl_2$ as a function of the displacement of the impurity along the ⟨110⟩ directions, with $r_{min}=3.32$ Å.

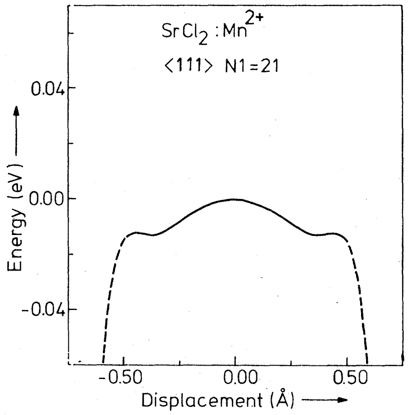

FIG. 12. Calculated potential energy of Mn^{2+} in $SrCl_2$ as a function of the displacement of the impurity along the ⟨111⟩ directions, with $r_{min}=3.14$ Å.

puting time by a factor 10. Then for one iteration step in the program for the ⟨111⟩ direction we needed about 2000 sec CP time on the Control Data Corp. Cyber computer of our university, which is too much to be manageable. The total energy changes about 0.001 eV in going from $N1+N2=131$ to 421.

Initially r_{min} was taken to be 5% less than the equilibrium distance in the corresponding pure crystal. r_{min}(Cl-Cl) is about the double of the Tosi-Fumi ionic radius of Cl^-. With this value of r_{min}(Cl-Cl) it turned out that, for all positions of the Mn^{2+}, the distance of some chlorine ions became equal to r_{min}. We decided to reduce r_{min} (Cl-Cl) to a value 10% less than the equilibrium distance in the pure $SrCl_2$ lattice. But now the development of a polarization catastrophe between the chlorines is no longer prevented. In the dashed regions of the curves in Figs. 11–13, we have a very large negative polarization energy, which is not balanced by the Coulomb and repulsion terms. The values of the displacement parameters for displacement of the impurity in the ⟨111⟩ direction, show that the ion numbered 2 in Fig. 3 tries to jump into the hole that is left by displacement of the Mn^{2+}. The ions in the plane formed by the ions 3, 4, and 6 are at r_{min} from the plane formed by the ions numbered 5, 7, and 8.

V. CONCLUSIONS

In view of the several uncertainties in the short-range potentials, which we are certainly aware of, the results are quite satisfactory. When we exclude the dashed regions in Figs. 11–13, we can conclude that the potential energy curve for dis-

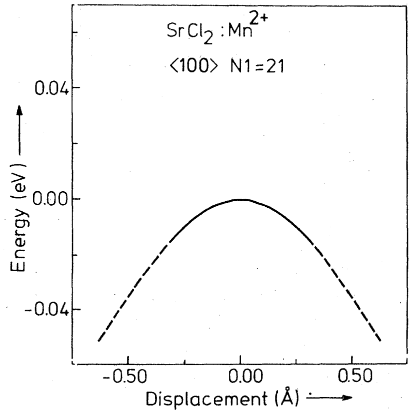

FIG. 11. Calculated potential energy of Mn^{2+} in $SrCl_2$ as a function of the displacement of the impurity along the ⟨100⟩ directions, with $r_{min}=3.14$ Å.

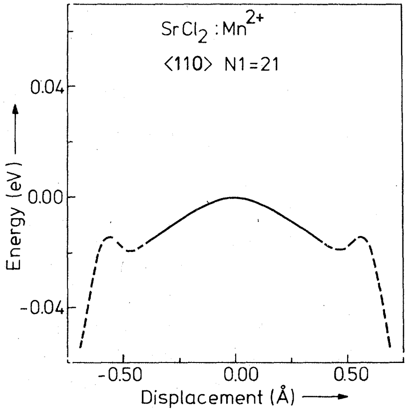

FIG. 13. Calculated potential energy of Mn^{2+} in $SrCl_2$ as a function of the displacement of the impurity in the ⟨110⟩ directions, with $r_{min}=3.14$ Å.

placement in the ⟨111⟩ direction is flat within 0.01 eV over a distance of 0.5 Å. In the other directions we have a similar behavior. The finer structure in the potential energy curve should not be considered as an evidence for the structure, that has been established experimentally, partly because of the occurrence of the "polarization catastrophe," and partly because of the unavailability of accurate input data.

ACKNOWLEDGMENTS

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