

Calculation of the shape of the potential well of Mn^{2+} in CaO, SrO, and BaO

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The shape of the potential energy well of Mn^{2+} as impurity in a number of alkaline-earth oxides is calculated, using the method of Hatcher and Dienes, for a polarizable-point-ion model. Potentials for the Mn-O, Ca-O, Sr-O, and Ba-O repulsion are derived. It is found that an effective charge of $Z = 1.6$ on the ions yields results that are in agreement with experiment. In CaO the Mn^{2+} ion occupies a substitutional site. In SrO the site of Mn^{2+} is also substitutional, but the potential well is very flat over a distance of 0.3 Å in the $\langle 111 \rangle$ direction. BaO: Mn^{2+} is found to be an off-center system. The off-center sites in the $\langle 111 \rangle$ and $\langle 110 \rangle$ direction are both 0.5 eV in energy below the ideal lattice site. The displacements of the impurity in the $\langle 111 \rangle$ and $\langle 110 \rangle$ directions are 0.6 and 0.8 Å, respectively.

I. INTRODUCTION

Off-center ions in crystals of the alkali halides have been subjected to extensive experimental and theoretical investigations (see, also, e.g., Refs. 1 and 2). Recent experiments on small substitutional ions in the alkaline-earth oxides have shown that off-center ions also occur in these crystals.³⁻⁵

Mostly, the experiments on the oxides have been done by using the electron-paramagnetic-resonance technique. The known off-center ions are of the paramagnetic type, such as Mn^{2+} and Cu^{2+} . However, contrary to the alkali halides, theoretical calculations of the form of the potential well which is seen by the impurity have not been carried out for the alkaline-earth oxides. In the last few years, more experimental information concerning the dielectric and elastic behavior of the alkaline-earth and transition-metal oxides at room temperature has become available. In this paper we present results of theoretical calculations of the shape of the potential well of substitutional Mn^{2+} in the crystals of CaO, SrO, and BaO.

II. EXPERIMENTAL INFORMATION

Matthew has pointed out early the important role of the difference in ionic radii of the impurity and host ions.⁶ The ionic radius of Mn^{2+} is 0.8 Å, whereas the radius of the alkaline earth ions increases from 0.99 Å for Ca^{2+} to 1.34 Å for Ba^{2+} . Consequently, an off-center system is highly improbable for CaO: Mn^{2+} , and possible for BaO: Mn^{2+} .

BaO: Mn^{2+} is known to be an off-center system, with stable positions of the Mn^{2+} along the eight equivalent $\langle 111 \rangle$ directions.^{4,5} EPR spectra of CaO: Mn^{2+} and of SrO: Mn^{2+} all exhibit cubic symmetry, indicating stable positions of Mn^{2+} at the substitutional lattice sites.⁷⁻¹⁰ Recently, Rubio *et al.*¹¹ have reported spectra of Mn^{2+} with tetra-

gonal site symmetry. However, because both cubic and tetragonal sites are observable at the same temperature, and the authors do not report any temperature dependence of the linewidth and relative intensity of the EPR lines, the tetragonal spectra cannot be caused by off-center Mn^{2+} .

SrO: Cu^{2+} is an off-center system.³ The off-center site can be observed with EPR at temperatures below 6 K. The ionic radius of Cu^{2+} is 0.72 Å, which is only 0.08 Å less than that of Mn^{2+} . We expect that the potential well of Mn^{2+} in SrO is very flat in the vicinity of the lattice site. Electric field effect experiments in EPR on $SrCl_2:Mn^{2+}$ support this assumption.^{12,13}

III. COMPUTATIONAL METHOD

The computational method, which we employed, is a slight variation of the method of Hatcher and Dienes,^{14,15} which was used by Wilson *et al.*¹⁶ for the calculations on KCl:Li⁺. This method uses a polarizable-point-ion (PPI) model for the description of the interactions between the ions. The PPI model gives reasonable results for the systems of the alkali halides.^{1,17} However, the validity of the results of these calculations becomes more questionable when the crystal binding becomes only partly ionic, as is the case for the alkaline-earth oxides.¹⁸ In the following we shall see, that we can overcome a great deal of the difficulties, due to covalency effects, by introducing an effective charge on the ions, which deviates from $2e$.

Below we summarize the method used in our calculations and the deviations as compared to the method employed by Wilson *et al.*¹⁶ The crystal is assumed to consist of polarizable point ions, labeled i , with charge e_i and polarizability α_i . We subdivide the crystal into two regions, I and II. In region I, in which the impurity is located, we have a number of ions, that are allowed to relax

from their lattice sites. Region II begins at the boundary of region I and includes an additional number of ions, that are not allowed to relax.

The expressions for the contributions to the total potential energy are given in Ref. 16 with the following exceptions. Firstly, the Coulomb energy is given by

$$\Delta_{\text{es}} = \sum_{i \in I} e_i \left(\sum_{\substack{m \in I \\ m > i}} \frac{e_m}{|\vec{r}'_i - \vec{r}'_m|} - \sum_{\substack{m \in I \\ m > i}} \frac{e_m}{|\vec{r}_i - \vec{r}_m|} \right) + \sum_{i \in I} e_i V(\vec{r}'_i - \vec{r}_i) + \sum_{i \in I} \left(e_i \sum_{\substack{m \in I \\ m > i}} \frac{e_m}{|\vec{r}_i - \vec{r}_m|} \right), \quad (1)$$

where $V(\vec{r}'_i - \vec{r}_i)$ denotes the difference in electro-

static potential of ion i , due to the displacement from its lattice site \vec{r}_i to the actual position \vec{r}'_i in an otherwise undisturbed lattice.

Secondly, the electric field is described by the following expression:

$$\vec{E}_i = \sum_{\substack{m \in I \\ m \neq i}} e_m \left(\frac{\vec{r}'_i - \vec{r}'_m}{|\vec{r}'_i - \vec{r}'_m|^3} - \frac{\vec{r}_i - \vec{r}_m}{|\vec{r}_i - \vec{r}_m|^3} \right) + \vec{E}_{\text{latt}}(\vec{r}'_i - \vec{r}_i), \quad (2)$$

and

$$\vec{E}_{\text{latt}}(\vec{r}'_i - \vec{r}_i) = -\text{grad}V(\vec{r}'_i - \vec{r}_i). \quad (3)$$

For a crystal with the rocksalt structure, the potential difference $V(\vec{r}'_i - \vec{r}_i)$ in (1) can be expanded in a Taylor series up to sixth order as

$$V_i(\vec{x}) = (Z_i e/a) \left[-114.5146(x_1^4 + x_2^4 + x_3^4) + 343.5439(x_1^2 x_2^2 + x_2^2 x_3^2 + x_3^2 x_1^2) - 126.6559(x_1^6 + x_2^6 + x_3^6) - 11399.0342(x_1^2 x_2^2 x_3^2) + 949.9195(x_1^4 x_2^2 + x_2^4 x_3^2 + x_3^4 x_1^2 + x_1^4 x_3^2 + x_2^4 x_1^2 + x_3^4 x_2^2) \right], \quad (4)$$

where

$$\vec{r}'_i - \vec{r}_i = a\vec{x}, \quad (5)$$

$Z_i e$ is the charge of ion i , and a is the lattice constant. The coefficients can be obtained by summation of the contribution of all ions to the corresponding derivatives of $1/r_i$ over a sufficiently large sphere in the crystal.

IV. DETERMINATION OF PPI MODEL PARAMETERS

A. Polarizabilities

The polarizabilities of the alkaline-earth ions and of oxygen were taken from the work of Tesson, Kahn, and Shockley.¹⁹ We did not find any values for the polarizability of Mn^{2+} in the literature. However, the values of ϵ_∞ and the lattice constants of the transition metal oxides MnO, CoO, and NiO are known (Table I). Assuming that the polarizability of the transition metal ions is linear in the cube of the ionic radius, we have fitted the function

$$\alpha_m(r) = Ar^3 + \alpha_{\text{O}^{2-}}, \quad (6)$$

to the experimental values of α_m . Here r is the ionic radius of the transition metal ion, $\alpha_{\text{O}^{2-}}$ the polarizability of oxygen and $\alpha_m = \alpha_+ + \alpha_-$ is calculated in accordance with the Clausius-Mossotti relation

$$(\epsilon_\infty - 1)/(\epsilon_\infty + 2) = (4\pi/3v_0)\alpha_m, \quad (7)$$

where v_0 is the volume of the primitive unit cell. We have used both Pauling and Goldschmidt values for the ionic radii.¹ Both sets of values give approximately the same value for the polarizability of O^{2-} , namely about 2.1 \AA^3 , which is of the right order of magnitude. The polarizabilities that were found, using the Pauling radii, are also given in Table I.

B. Repulsion parameters

The main difficulties in these calculations are caused by the absence of experimentally verified expressions for the repulsion potentials over a

TABLE I. Some experimental data for MnO, CoO, and NiO.

	MnO	Reference	CoO	Reference	NiO	Reference
$\frac{1}{K}$ (10^{11} dyn/cm ²)	15.4	20				
r_0 (Å)	2.222	20	2.13	21	2.0885	21
ϵ_∞	4.95	21	5.3	21	5.7	21
α_+ (Å ³)	0.9(12)		0.6(65)		0.5(85)	
α_- (Å ³)	2.1		2.1		2.1	

TABLE II. Experimental data for the alkaline earth oxides.

	CaO	Reference	SrO	Reference	BaO	Reference
$1/K$ (10^{11} dyn/cm ²)	11.4	24	8.8	24	6.1	20
r_0 (Å)	2.406	24	2.58	24	2.77	20

range of values for the interionic distance. For the alkali halides, a lot of work has been done on these potentials, and there are a number of papers which contain calculations on off-center systems employing various repulsion potentials.^{16,17} It was found¹⁷ that a simple Born repulsion potential with nearest-neighbor interaction is sufficient to predict the off-center behavior of KCl:Li⁺, provided that the parameters are calculated from low-temperature experimental data.

For a crystal with the rocksalt structure, the parameters B and ρ of the Born potential

$$\phi_{\pm}^{\text{SR}}(r) = B \exp(-r/\rho) \quad (8)$$

can be determined from the experimental values of the compressibility,²² by solving

$$\left. \frac{dU}{dr} \right|_{r_0} = \frac{\alpha_M Z^2 e^2}{r_0^2} + 6\phi'(r_0) = 0 \quad (9)$$

and

$$\left. \frac{18r_0}{K} = \frac{d^2U}{dr^2} \right|_{r_0} = -\frac{2\alpha_M Z^2 e^2}{r_0^3} + 6\phi''(r_0) \quad (10)$$

for $\phi'(r_0)$ and $\phi''(r_0)$, where SR stands for short range.

Here, $U(r)$ is the static energy per unit cell for nearest-neighbor separation r , r_0 the equilibrium value of r , K the compressibility, Ze the magnitude of the charge of an ion, and α_M the Madelung constant.

We determined the parameters B and ρ from the experimental data in Tables I and II. These parameters depend on Z , as can be seen from (9) and (10). By choosing $Z=2$ for MnO, we have made a conservative choice, with regard to a possible off-center behavior, because a smaller value of Z would yield a weaker repulsion between Mn and O, thus making an off-center system more probable.

As is known from the work of Wilson *et al.*,¹⁶ it is possible that a "polarization catastrophe" develops, when one ion is allowed to move close to the impurity. This arises because the Born potential is finite at zero separation of the ions, while the polarization and Coulomb energy become infinitely negative. In order to avoid this, a quasi-infinite potential of the form

$$\phi(r) = 100\,000(1 - r/r_{\text{min}}) \text{ (eV)}, \quad (11)$$

is added to the repulsion potential, when the distance between the ions is smaller than some mini-

mum distance r_{min} . r_{min} is chosen usually to be a little less than the sum of the ionic radii of a pair of ions.

C. Ionic charge Z

Because the alkaline earth oxides are partly covalent it is not clear what value should be taken for the ionic charge in the PPI model. As a first approximation, one could take $Z=2$. Secondly, Son, Bartels, and Vetter^{23,24} have performed measurements of the compressibility and its pressure derivative of the alkaline-earth oxides. The authors have tried to fit a Born potential with nearest-neighbor interaction to the experimental data. This was only possible in a consistent way, when the ionic charge Z was taken equal to ≈ 1.6 . However, in that case the predicted binding energy is too small, as compared to the thermochemical binding energy.

Effective charges are frequently used in lattice

TABLE III. Input data for calculations of AO:Mn²⁺ ($A = \text{Ca, Sr, Ba}$).

	Lattice constant (Å)	Polarizabilities (Å ³)	
		α_+	α_-
CaO	4.806	1.1	1.8
SrO	5.16	1.6	2.0
BaO	5.54	2.5	2.5
Repulsion parameters			
$B(\text{Mn-O}) = 9.6035 \times 10^{-10}$ erg			
$\rho(\text{Mn-O}) = 0.3584$ Å			
Parameter	Z	2.00	1.6
B (Ca-O) (erg)		9.2027×10^{-10}	4.640×10^{-9}
ρ (Ca-O) (Å)		0.3850	0.2785
r_{min} (Å)		1.91	1.91
B (Sr-O) (erg)		9.3943×10^{-10}	5.0148×10^{-9}
ρ (Sr-O) (Å)		0.4063	0.2933
r_{min} (Å)		1.91	1.91
B (Ba-O) (erg)		6.619×10^{-10}	2.977×10^{-9}
ρ (Ba-O) (Å)		0.4594	0.3343
r_{min}		1.91 ^a	2.12/1.91 ^a

^aThe polarization catastrophe occurs here. The energy depends on the choice of r_{min} . In Figs. 2 and 3 the results for $r_{\text{min}}=2.12$ are given. 2.12 is equal to the sum of the ionic radii of Mn²⁺ and O²⁻, and also 0.1 Å less than the nearest-neighbor distance in MnO.

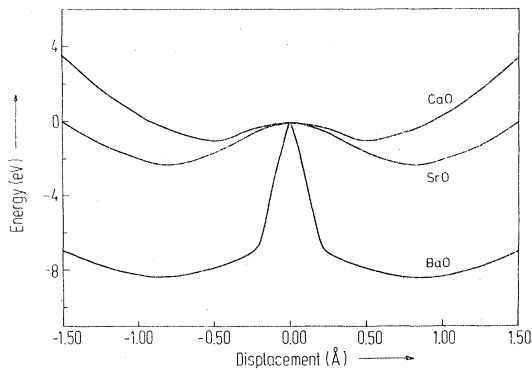


FIG. 1. Potential energy as a function of displacement of the Mn^{2+} ion along the $\langle 111 \rangle$ directions for $Z=2$. The potential energy at the lattice site is defined equal to zero.

dynamical models. However, often the physical significance of them is not clear. We consider the value $Z \approx 1.6$ as an experimentally determined parameter.

V. RESULTS AND DISCUSSION

All calculations have been carried out with seven relaxable ions in region I. For displacements of the impurity in the $\langle 100 \rangle$ and $\langle 111 \rangle$ direction one needs then five, and in the $\langle 110 \rangle$ direction seven displacement parameters.¹⁶ It is not sensible to include more relaxable ions, because of the crudeness of the PPI model for the substances under consideration. For the total number of ions in region I+II, we have taken 93. The total energy is then calculated within an error of ≈ 0.001 eV. The input values for the parameters are given in Table III.

To start with, we calculated the shape of the po-

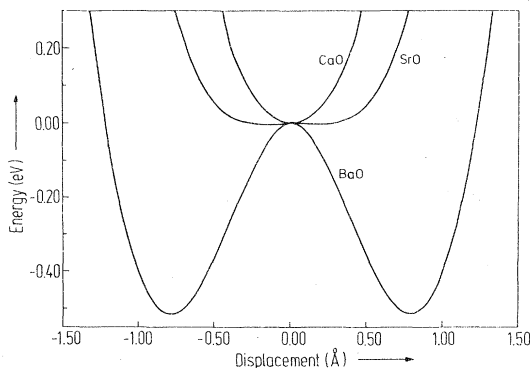


FIG. 2. Potential energy as a function of displacement of the Mn^{2+} ion along the $\langle 111 \rangle$ directions for $Z=1.6$. The potential energy at the lattice site is defined equal to zero.

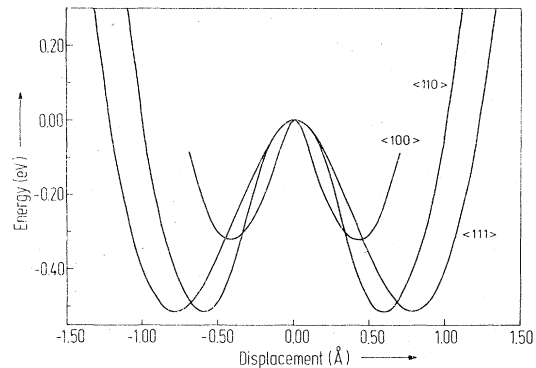


FIG. 3. Potential energy as a function of displacement of the Mn^{2+} ion in BaO along the $\langle 100 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$ directions for $Z=1.6$. The potential energy at the lattice site is defined equal to zero.

tential well for all systems with displacements of Mn^{2+} along the $\langle 111 \rangle$ direction. This direction is most probable for finding an off-center system. The results are given in Fig. 1.

Clearly, these results are not acceptable. The large negative values of the total energy are due to the electrostatic terms, i.e., the ions attract each other too strongly. Consequently, we have to reduce the value of Z .

The results for $Z=1.6$ are given in Fig. 2. With this value of Z , we have an off-center system for BaO: Mn^{2+} , the potential energy curve is flat for SrO: Mn^{2+} , and CaO: Mn^{2+} is definitely not an off-center system.

Next, we looked in the BaO: Mn^{2+} case at the depth of the energy minima as a function of the direction of displacement of the Mn^{2+} ion. It turns out, that we cannot predict any difference between the $\langle 111 \rangle$ and $\langle 110 \rangle$ direction (Fig. 3).

From the temperature dependence of the EPR linewidth an activation energy of 0.05 eV has been measured.⁴ Thus, there should exist a potential barrier of this order of magnitude between the $\langle 111 \rangle$ sites. Apparently, the PPI model and the employed parameters are not accurate enough to account for such a small difference in potential energy. However, on the whole the results are quite satisfactory.

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