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Crystal-Field Effects and the Migration of Transition-Metal Ions in AgCl†

A. P. Batra, J. P. Hernandez, and L. M. Slifkin
Department of Physics and Astronomy, University of North Carolina, Chapel Hill, North Carolina 27514

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The diffusion of a set of consecutive divalent transition-metal ions has been measured in AgCl. Their high-temperature activation energies are found to span the range from 1 to 2 eV and to exhibit a systematic dependence on the number of electrons in the *d* shell. The relative migration energies can be quantitatively accounted for in terms of the electronic contributions to the energies of the ions, in the normal and activated positions, resulting from crystal-field splittings.

An understanding of the properties of impurity ions in ion crystals, such as the silver halides, requires a consideration of the effect of the crystalline field on the electronic states of these ions. In this Letter, this effect is shown to be reflected in the activation energies for the substitutional migration of the first-row transition elements in silver chloride. Although these notions have been previously used in interpreting the partitioning of transition elements in duplex scales on oxidized alloys,[1] the present results are believed to demonstrate clearly, for the first time, a quantitative correlation between an ion transport phenomenon and the effects of the crystal field at the various sites in a simple halide salt.

The activation energies for diffusion in AgCl of V^{2+}, Cr^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} (all $3d^n$ ions) have been determined from the temperature dependence of the diffusion coefficient as measured by the conventional tracer-sectioning technique.[2] (The details of the measurements will be given elsewhere.) These energies, along with those previously reported for the diffusion of divalent manganese[3] and zinc,[4] are presented in Table I. Only the values derived from least-squares fits to the high-temperature data are shown since the values in that range may be taken to be insensitive to the codiffusion of polyvalent impurities in the tracer solution and to residual impurities in the host crystal, and thus are deemed as quite accurate for the purpose of comparison. It may be noted that the temperature range for the Ni^{2+} measurements is small; this is due to the less-sensitive surface counting method required by the

TABLE I. Diffusion of first-row transition-metal ions in AgCl.

Tracer	Configuration	Temperature range (°C)	Diffusion activation energy (eV)	$H_m^{\text{solute}} - H_m^{\text{Mn}^{2+}}$ (eV)		
				Expt. (±0.03 eV)	Avg. calc.	Individual ion calc.
V^{2+}	$3d^3$	352–441	2.08	0.90	0.88	0.96
Cr^{2+}	$3d^4$	325–440	1.25	0.07	0.07	0.11
Mn^{2+}	$3d^5$	249–420	1.18	0	0	0
Fe^{2+}	$3d^6$	274–442	1.26	0.08	0.03	0.03
Co^{2+}	$3d^7$	328–441	1.39	0.21	0.27	0.17
Ni^{2+}	$3d^8$	393–441	1.88	0.69	0.88	0.72
Zn^{2+}	$3d^{10}$	352–441	1.01	≤ 0.18	0	0

weak β emission, coupled with the relatively chemically impure tracer solution supplied by the manufacturer.

The diffusion activation energy for any divalent ion includes contributions due to the formation of a cation vacancy, from the activation energy of solute-vacancy interchange, and from impurity-vacancy binding (the temperature dependence of correlation effects may be neglected here since the jump frequency for the divalent solute-vacancy exchange may be assumed to be small in comparison with other pertinent vacancy frequencies). Impurity-vacancy binding energies have been obtained from ionic conductivity measurements. The measured values of 0.245 eV,[5] or 0.266 eV,[6] for Mn^{2+} and 0.236 eV[5] for Ni^{2+} differ by only a few hundredths of an electron volt. Recent measurements give a tentatively similar value[7] for Fe^{2+} and Co^{2+}. Thus it seems reasonable to assume that the $3d^n$ ion-vacancy binding energies in AgCl are all approximately the same. The only exception is for Zn^{2+} where values of 0.5 to 0.6 eV have been observed[4,5] (this anomaly is also observed in NaCl[8]).

Given these considerations, the solute migration energies (H_m^{solute}), relative to that for Mn^{2+} ($H_m^{Mn^{2+}}$), have been obtained from their diffusion-activation-energy differences and the values are also given in Table I. We now show that these values agree rather well with those calculated on the assumption that differences in the migration barriers among the set of $3d^n$ divalent ions are purely due to the effects of crystal-field splittings on the electronic contribution to the energies of the ions in the normal (substitutional) and activated (assumed to be the interstitial) positions.

The calculations use the strength of the crystal field, with the impurity at the substitutional position, obtained from analyses of the optical absorption spectra due to the impurities in AgCl. Such analyses have assumed an octahedral symmetry, ignoring explicit perturbations due to a nearest cation vacancy. For our purposes the vacancy must exist since it occupies the position to which the impurity ion will jump. At the temperatures at which the optical spectra were carried out, the impurities and vacancies are largely associated. However perturbations to the crystal field due to the vacancy are expected to be small (2% in the point-ion approximation) and are implicit in the values obtained from analyses of optical data.

With the impurity in the activated position the crystal field is not known and there is the added complication of two cation vacancies (the original and final positions of the diffusing ion). Therefore instead of the one known parameter (octahedral case) there are several unknown parameters for the crystal field in this case. In order to minimize parametrization of the problem, the crystal field, in this case, has been taken to be the one appropriate to point ions for the crystal with two vacancies, multiplied overall by a single unknown parameter characterized by γ, which is defined as follows:

$$\frac{(V_4^0)_{\text{interstitial}}}{(V_4^0)_{\text{substitutional}}} = -\frac{2}{9}\left(\frac{2}{\sqrt{3}}\right)^5 \gamma,$$

where V_4^0 is part of the interaction potential with angular variation given by the Legendre polynomial of order four, and the factor $2/\sqrt{3}$ comes from the ratio of the distances to the closest ions in the normal and interstitial positions. If the host crystal were made up by point ions γ would equal 1 with the two vacancies present and zero if there were no vacancies. Note, therefore, that results with $\gamma = 0$ represent relative stabilization energies among the impurity ions for the substitutional position.

Since Mn^{2+} and Zn^{2+} have ground S states there will be no crystal-field splitting; hence migration energy barriers for other $3d^n$ ions, relative to Mn^{2+} or Zn^{2+}, are obtained directly from the crystal-field–splitting calculations. Mixing of F and P terms, where appropriate, has been taken into account but spin-orbit effects have been neglected since they are estimated to be a few hundredths of an electron volt at maximum.

The results of the calculations are presented in Fig. 1 which shows the energy barriers relative to that of Mn^{2+} or Zn^{2+} versus the parameter γ, in the range 0 to 0.6. This figure results from the approximation, for ease of presenting the results, that the crystal-field parameter Dq (for the octahedral case) is the same for all ions and has the average value 680 cm^{-1} (see Sliker[9] and Koswig, Retter, and Ulrici[10]) and F-P term energy differences are all 1.52 eV (see Ref. 9 and Condon and Shortley[11]). A best fit to the measured results is obtained for $\gamma = 0.43$ and the corresponding values of the migration-energy differences are listed in Table I under "average calculation." A similar calculation which takes into account the variations among the ions of the parameters Dq,[10] $\langle r^2\rangle$, $\langle r^4\rangle$,[12] and F-P energy difference[9,11] will be shown in detail elsewhere. It gives best-fit results for $\gamma = 0.5$ which are also listed in Table I.

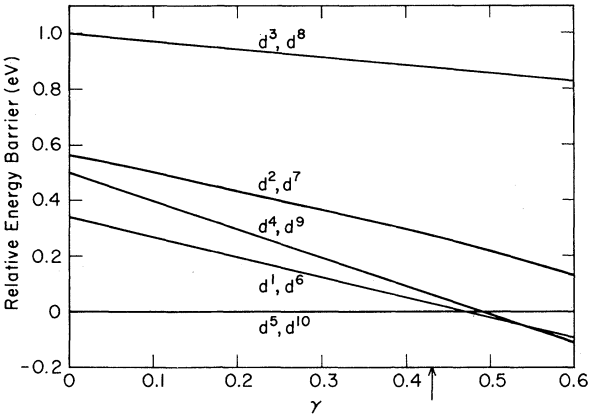

FIG. 1. Energy barrier for impurity migration in AgCl relative to that for Mn^{2+} or Zn^{2+} as a function of a crystal-field parameter γ for the "average calculation," as defined in the text. The arrow indicates the value of γ for the best fit.

As may be noted, the main effect of taking some detailed differences among the ions into account is to cause a splitting between d^n and d^{5+n} ions, thus reproducing the experimental difference of ~ 0.2 eV between V^{2+} and Ni^{2+}, along with the experimental ordering for them.

The agreement between calculation and experiment is excellent and appears to represent a first demonstration of the role of electronic structure in affecting the mobility of ions in an ionic crystal. This strongly suggests the desirability of including crystal-field effects in the theory of diffusion in ionic crystals.

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Dynamics of Electron Localization in Dense Helium Gas*

K. W. Schwarz† and B. Prasad
Department of Physics and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637

(Received 9 October 1975)

A new experiment shows that in dense, cold helium gas an excess electron can occupy either a distinct group of highly mobile states or another group of relatively immobile, presumably localized states. The rapid decrease in average mobility with increasing gas density observed in previous experiments arises primarily from an exponential increase in the lifetime of the electron in the localized states.

A helium atom scatters low-energy electrons much like a hard sphere. An excess electron in a gas of helium atoms therefore acts approximately as a particle in a potential consisting of randomly placed billiard balls. Since it is not difficult to achieve gas densities and temperatures such that the interatomic distance is comparable to the thermal wavelength of the electron, this system provides an elegant and experimentally flexible prototype for the study of electronic states in a disordered material.

Interest in this system originated with the early mobility measurements of Levine and Sanders,[1] who showed that as the gas density is increased beyond $n \approx 10^{21}$ cm^{-3}, the average mobility $\bar{\mu}$ of an excess electron decreases precipitously from