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and a galvanometer. It was found that the photoconductivities of the samples with relatively large Mn concentrations and distinctly observable Mn emissions are by far smaller than those of the samples with relatively small Mn concentrations and scarcely observable Mn emissions.

Further work on this problem is in progress, and the sensitization mechanism will be discussed later.

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Crystal Growth and Coercive Forces of Variously Prepared Ni Powders

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An increase in the coercive force H_c of a crystallized material by growth in a magnetic field (m.f.) can most readily be attributed to an influence in the incorporation of new material into the substrate crystal lattice.[1] Since this deposition reaction is probably the most obscure of the sequence of reactions comprising crystal growth, any correlation between H_c and growth in a m.f. may be useful in clarifying the incorporation process.

Experimentally, a freshly prepared, cold, aqueous solution variously containing 0.05–1M $NiSO_4$, 1–6M NH_3, 0.5–1M $(NH_4)_2SO_4$, and a reducing agent, 0.05–1M NaH_2PO_2(**I**) or 100–500 psi H_2pp, was sealed into a glass tube or SS bomb and placed in an oil bath controlled at 185–225±5°C. Ni metal powder formed within an hour in this temperature range. Reductions were performed in magnetic fields of 0–1200 oersteds using a permanent magnet.

Reduction by **I** outside a m.f. (neglecting the earth's field) gave irregular stringed agglomerates of metal particles, 1–3 microns wide by 10–50 microns long; while reduction in a 1200 oersted field gave smooth, straight, 1–3 by 50–500 micron agglomerates (Fig. 1). All agglomerates were chains of 1–3 micron particles which were each composed of several primary particles. Variation in reagent concentrations and temperature did not noticeably affect agglomeration. X-ray examination of **I**-prepared powders showed no appreciable particle orientation. Products contained 2 percent P. Reduction by H_2 both in and outside a field gave 10–50 micron irregular flocs of 1-micron primary metal particles.

FIG. 1. Ni powder prepared by reduction of aqueous $NiSO_4-NH_3-(NH_4)_2SO_4$ solution with NaH_2PO_2 in a 1200-oersted magnetic field. Magnification = 75 ×.

Coercive forces (in oersteds) at ambient temperature were: 17±5 for H_2-prepared powder produced in and outside a field; 75±5 for **I**-prepared powder produced outside a field (see Weil and Marfoure[2]); and 110±10 for **I**-prepared powder produced in a 1200-oersted field, thus far below the H_c of 3150 predicted for Ni powder with shape anisotropy.[3] Any stringed agglomerates were previously magnetically aligned parallel to the measuring field. The transition in the direction of easy magnetization in Ni from $\langle 111\rangle$ to $\langle 100\rangle$ directions at about 200°C[4] may obscure these results, but reduction with **I** at 185° and 225° gave powders with similar H_c values.

The increase in H_c when reduction with **I** occurred in a m.f. indicates that the field affects crystal growth, but conclusions as to modification of growth rate or crystal habit were not permitted. The apparent lack of effect of a m.f. on H_c in growth by H_2 reduction compared to the marked effect in **I** reduction suggests that the deposition mechanisms in the two cases may be qualitatively different.

I-prepared powders were magnetically saturated by only a 600-oersted field (compared to 2100 oersteds for a multidomain particle), but deductions based upon saturation[5] are probably not applicable to the impure powders prepared here. Experimental error does not warrant a conclusion about saturation for the H_2-prepared powder.

The marked variation in particle agglomeration in **I**- and H_2-prepared powders cannot be discussed since the factors affecting colloid stability,[6] e.g., double layer repulsion potentials and particle concentrations, are completely unknown for these systems at the reaction temperatures. Accentuation of linear agglomeration in **I**-prepared powder by a m.f. of only 5 oersteds suggests that magnetic forces directed particle agglomeration.[7] Linear agglomeration because of a repulsion potential minimum along a "biparticle" axis[8] seems less likely.

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Calculation of Electrostatic Binding Energies in Systems of Isotropic Ions

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It has been shown[1] that ionic polarizabilities lead to substantial contributions to binding energies in cases where the structure is such that large electric fields exist at the ions. The usual computation for the electrostatic part of the binding energy involves a determination of the induced moments from polarizabilities and the computed electric fields at each ion, followed by the summation of pair potentials between ions and induced dipoles, and the work of formation of the dipoles.[1] Quadrupole and higher terms, which may be important in some cases, have been ignored because of lack of information regarding the induced multiple moments.

For isotropic ions, the general expression to induced dipole terms may be written

$$V_e=\tfrac{1}{2}\Sigma'\frac{Z_iZ_je^2}{r_{ij}}-\Sigma'\frac{Z_ie}{r_{ij}^3}(\boldsymbol{\mu}_j\cdot\mathbf{r}_{ij})-\tfrac{1}{2}\Sigma'\left\{\frac{3}{r_{ij}^5}(\boldsymbol{\mu}_i\cdot\mathbf{r}_{ij})(\boldsymbol{\mu}_j\cdot\mathbf{r}_{ij})-\frac{(\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j)}{r_{ij}^3}\right\}+\Sigma\frac{\mu_i^2}{2\alpha_i},\quad(1)$$

where the sums for the first three terms are over all i and j except $i=j$, Z_ie is the charge on the ion i, $\boldsymbol{\mu}_i$ is the induced moment, and $\mathbf{r}_{ij}$ is the vector pointing from the ion i to the ion j. The four terms correspond respectively to charge-charge, charge-dipole, and dipole-dipole potentials, and the work of formation of the induced dipoles.

For cases involving more than two ions, direct computations from (1) became tedious, especially because of the last two sums, which involve second-order terms in μ. To simplify this equation, we may insert α_iE_i for one of the μ_i in the last term. In vector notation, recalling that the field and dipole directions coincide, one obtains

$$\frac{\mu_i^2}{2\alpha_i}=\frac{(\boldsymbol{\mu}_i\cdot\mathbf{E}_i)}{2}=\tfrac{1}{2}\sum_j\left\{\frac{Z_je(\boldsymbol{\mu}_i\cdot\mathbf{r}_{ij})}{r_{ij}^3}+\frac{3(\boldsymbol{\mu}_{ij}\cdot\mathbf{r}_{ij})(\boldsymbol{\mu}_j\cdot\mathbf{r}_{ij})}{r_{ij}^5}-\frac{(\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j)}{r_{ij}^3}\right\}.\quad(2)$$

Substituting this into (1) and rearranging, we find

$$V_e=\tfrac{1}{2}\Sigma'\frac{Z_iZ_je^2}{r_{ij}}-\tfrac{1}{2}\Sigma'\frac{Z_ie(\boldsymbol{\mu}_j\cdot\mathbf{r}_{ij})}{r_{ij}^3}.\quad(3)$$

This may be written

$$V_e=\tfrac{1}{2}\Sigma_iZ_ie\varphi_i,\quad(4)$$

where

$$\varphi_i=\sum_j\left\{\frac{Z_je}{r_{ij}}-\frac{(\boldsymbol{\mu}_j\cdot\mathbf{r}_{ij})}{r_{ij}^3}\right\}.\quad(5)$$

Numerical computations are simpler with Eq. (3) because the second sum is just one-half the second sum of (1), and there are no terms above first power in μ.

It is seen that φ_i is the potential at the ion i produced by all the other ions and induced dipoles in the final configuration of the system. Thus, when the effects of the induced dipoles are included in the expression for φ_i, Eq. (4), which is rigorously correct for a system of nonpolarizable particles, also yields the correct result for isotropic polarizable particles. It is anticipated that this result is general, i.e., that multipolar contributions need be included only in φ_i to make binding energy computations of a higher order of accuracy. This would require knowledge of multipolar polarizabilities and solution of the electric field problem to appropriate derivatives of E. Although the multipolar coefficients are not yet avaialble, it appears that in certain instances experimental nuclear electric quadripole resonance data might be useful in obtaining the quadrupole terms.

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Structure and Calculation of the Binding Energy of Gaseous Alkali Halide Dimers

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As the properties of alkali halide monomers can be explained on the basis of an electrostatic model,[1] expressions have been developed for a proposed dimer structure, employing the formulation of an accompanying note[2] for the binding energy, which includes all Coulombic and induced dipole interactions. Because the leading terms are the Coulomb interactions, it is evident that the energetically favored configuration of the ions will be the symmetrical planar arrangement of Fig. 1. Proceeding as usual,[3] the the electric field problem was solved for this structure. The field equations are

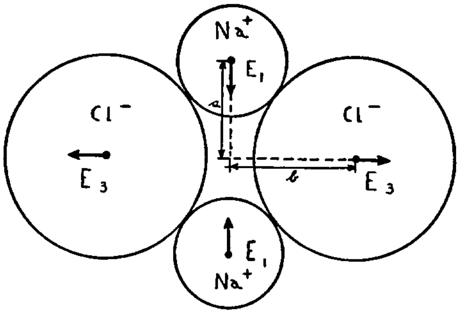

FIG. 1. Proposed structure for the NaCl dimer. Arrows are field vectors. To scale.

$$E_1(1+\alpha_1/4a^3)=Ze\{2a/(a^2+b^2)^{3/2}-1/4a^2\}+6ab\alpha_3E_3/(a^2+b^2)^{5/2},\quad(1)$$

$$E_3(1+\alpha_3/4b^3)=Ze\{2b/(a^2+b^2)^{3/2}-1/4b^2\}+6ab\alpha_1E_1/(a^2+b^2)^{5/2}.$$

E_1 and E_3 are the magnitudes of the electric field intensities at the cation and anion, respectively, α_1 and α_3 are the corresponding ionic polarizabilities, $2a$ and $2b$ are the intercationic and interanionic separations, Ze is the ionic charge, and units are cgs. The directions of the electric field and induced dipole vectors are shown in Fig. 1.

The expression for the electrostatic part of the binding energy is

$$V_e=Ze(\varphi_1-\varphi_3),$$

$$\varphi_1-\varphi_3=-Ze\{4/(a^2+b^2)^{1/2}-1/2a-1/2b\}+\{1/4a^2-2a/(a^2+b^2)^{1/2}\}\alpha_1E_1+\{1/4b^2-2b/(a^2+b^2)^{1/2}\}\alpha_3E_3.\quad(2)$$

As an example, numerical computations have been carried out for $(NaCl)_2$. Employing the polarizability values given recently,[4] it was found that the maximum binding energy at constant internuclear separation, $r=(a^2+b^2)^{1/2}=2.59$ A, was obtained with $b/a=1.35\pm0.05$ A, which corresponds to an apex angle of 105±2° at the sodium ion. The effects upon the angle of the London attractive forces,[5] and the short range quantum-mechanical repulsions,[6] between the anion pairs and between the cation pairs were found to be negligible. Therefore it was necessary to include only the Coulombic and induced dipole interactions in the determination of the angle. The energy of formation of the dimer from the ions was calculated as a function of r. Neglecting the zero-point energy, estimated to be a few hundredths of an electron volt, the energy of formation of the dimer from ions at 0°K may be written

$$V=V_e+V_r+V_L,\quad(3)$$

where V_e is the electrostatic binding energy, V_r is the repulsion enregy, and V_L is the London attractive energy. Following Rittner,[1] the repulsive potential function $A\exp(-r/\rho)$ was used, so $V_r=4\,A\exp(-r/\rho)$. The recent value,[7] $r_e=2.3606$ A, was employed in determining $A=2530$ ev, and $\rho=0.311$ A. V_L, computed with the new polarizability values,[4] and the London constants from Rittner's work, turned out to be very small. The minimum energy $V=-13.12$ ev, was obtained at $r=2.59\pm0.01$ A. Employing the recent parameters[4, 7] and Rittner's equations, a binding energy of 5.63 ev was obtained for the NaCl monomer. This is equal to the experimental value obtained in the usual manner from the dissociation energy of the molecule into neutral atoms, the first ionization potential, and the electron affinity.[8] Then at 0°K for the reaction

$$2NaCl=(NaCl)_2,$$

$$\Delta E=-1.86 \text{ ev}.$$

Experimental results for the structure and binding energies of the dimers are not yet published, but some indications have