**THEORY OF THE REACTION BETWEEN
ALKALI METAL AND ALKALI HALIDES WITH
APPLICATION TO THE SYSTEM K-KCl**

**ATOMIC ENERGY RESEARCH DEPARTMENT
NORTH AMERICAN AVIATION, INC.**

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ABSTRACT

The properties of a system consisting of colloidal alkali metal particles in thermal equilibrium with a crystalline alkali halide are considered in detail, with particular reference to the system K-KCl. It is shown that in the system K-KCl, the particles most probably are about 20 Å in size and consist of liquid metal compressed about 15 per cent by surface tension. A theory of the three-phase reaction between a liquid metal, vapor, and crystal is developed more completely than heretofore and is shown to be in quantitative agreement with recent experimental results. A value of -0.10 ev found by Rögner for W_f , the work done in forming an F-center from a K atom in the vapor, is shown to lead to quantitative inaccuracy in the predicted ratio of F-center to vapor concentration, whereas a value of -0.5 ev deduced from more recent experiments leads to an acceptable value for this ratio. A theoretical calculation of W_f is reviewed, and it is concluded that the existing inaccuracy is due to an unsatisfactory value for χ , the electron affinity of KCl. A recent report that the additive coloring process is not reversible is discussed, and it is shown that further experiments are essential before the mechanism and the reversibility of the additive coloring process can be considered established. It is concluded that the heats of reaction which are observed are in substantial agreement with a theoretical prediction based on the assumption that one reactant is colloidal metal embedded in the alkali halide crystal but that current interpretations of the resulting optical absorption phenomena require revision to incorporate a more realistic view of the physical state of the metal in these particles.

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I. INTRODUCTION

Recent progress in the study of lattice defect coagulation in radiation-damaged and additively-colored alkali halide crystals has suggested that the coagulation occurs in a two-step process.¹ In the first step, color centers are destroyed; in the second, the intermediate centers which result become aggregated into subultramicroscopic colloidal alkali-metal particles, whose optical absorption properties are described by the well-known theory of G. Mie.² Properties of colloidal aggregates in additively-colored alkali halides have been extensively investigated.^{3,4} Similar effects in radiation-damaged crystals were studied as early as the year 1905,⁵ and recently have been investigated by Przibram and co-workers⁶ and by the author.⁷ In connection with this study, an estimate recently was made⁸ of the heat of reaction between colloids and F-centers in KCl, according to the following process: a potassium atom, dissociated from a colloidal particle embedded in a potassium chloride crystal, is added to the KCl lattice in the form of a K^+ ion and an F-center electron. A pair of vacancies (dissociated) is created to maintain thermal equilibrium. It was assumed that the strain interaction between particle and lattice is negligible. The result obtained was about 0.7 ev higher than a recent approximate experimental value,³ but this discrepancy was not considered sufficient, in view of the several uncertainties inherent in the calculation, to serve as an argument against the theory that colloidal particles are partially responsible for the absorption phenomena observed in these crystals.

Greater accuracy should be expected of the theory than was observed, however, and the problem has been examined further in an effort to increase the quantitative agreement between theory and experiment. In the course of this investigation several questions of fundamental importance have arisen, partially occasioned by a recent paper in the Russian literature concerning the mechanism of the additive-coloring process. Some of these questions will be discussed in later sections of this report. First, however, the theory from which the heat of reaction between colloidal particles and F-centers may be calculated will be developed in a somewhat more complete form than has been presented previously, and it will be shown that the disagreement between this theory and experiment is largely eliminated if the most appropriate recent experimental results are employed. This conclusion, then, lends support to the

colloidal particle theory of absorption phenomena mentioned above and clarifies the problem of the reaction between alkali metal and alkali halide crystals.

II. THE PHYSICAL STATE OF COLLOIDAL K IN KCl

It is worthwhile to digress briefly, to consider the physical state in which the colloidal metal particles are most likely to be found, and the dependence of this state on particle size and geometry. The conclusions of this section are directly related to the optical properties to be expected of the crystal containing colloids, since these properties are determined mainly by the complex index of refraction of the metal in the particles, which in turn is a function of their physical state.

One notes immediately that the molecular volume of crystalline KCl is $2 \times (3.14)^2 = 62 \text{ \AA}^3$, while the volume occupied by an atom of K in the metal is $(5.25)^3/2 = 72.5 \text{ \AA}^3$; thus there is insufficient room for particle precipitation to occur in KCl simply as a result of the coagulation of F-centers, unless the lattice is appreciably strained or the particle is compressed by about 14-1/2 per cent. The compression may occur in the absence of lattice strain in the surrounding KCl only if the surface energy of the particle is high enough. We therefore shall make an estimate of the surface energy of small colloidal particles of potassium.

To do so, it is necessary to fix the size of the particles under consideration. Evidence obtained thus far³ suggests that 50 Å is an upper limit for the size of the particles with which we are concerned. We shall find below that strain interaction with the KCl lattice is negligible for 20 Å particles, a size consistent with the above limit and with other information regarding the particles' behavior.³ Let us consider, therefore, a spherical particle of potassium, whose radius is 10 Å.

We consider first the possibility that particles of this size are in a liquid state. The surface tension γ of liquid potassium is about $400 \text{ dynes} \cdot \text{cm}^{-1}$; this results in a pressure within the spherical droplet of $\frac{2\gamma}{r} = 8.0 \times 10^3 \text{ kg} \cdot \text{cm}^{-2}$. According to curves obtained by Bridgeman,^{9a} potassium under a pressure of $8000 \text{ kg} \cdot \text{cm}^{-2}$ melts at 152.5°C . If the surface tension of the spherical droplet were the only factor influencing the melting point, therefore, we should find the particles in a solid state at all temperatures below 150°C .

An additional effect, however, results from the interfacial energy between the liquid and solid phases, combined with the large curvature of the surface of a solid phase contained within the minute droplet. This problem is treated in detail by Epstein,¹⁰ who derives an expression for the change produced by interfacial curvature in the temperature of the solid-liquid transformation:

$$\Delta T = \frac{\sigma C T}{\rho \ell_m}, \quad \dots (1)$$

where T is the temperature of the solid-liquid transformation under the prevailing constant pressure ($8000 \text{ kg} \cdot \text{cm}^{-2}$ in our case) in the absence of a curved interface; C is the curvature of the interface, which is given here by $-\frac{2}{r} = -2 \times 10^7 \text{ cm}^{-1}$ for the largest particle which may exist in a 20 Å droplet; σ is the interfacial energy for the surface between the solid and liquid phases; ρ is the density of the solid phase, $0.87 \text{ gm} \cdot \text{cm}^{-3}$; and ℓ_m is the heat of fusion per gram, 6.5×10^8 ergs. A value for σ apparently is not available directly from experiment, but one may be estimated from a correlation of interfacial energies in other metals by Turnbull,¹¹ who finds that the gram-atomic surface energy σ_g is given fairly accurately by

$$\sigma_g = \frac{1}{2} \ell_m \quad \dots (2)$$

for a wide range of metallic substances. The gram-atomic surface energy is converted to the interfacial energy per cm^2 by the relation

$$\sigma = N^{-1/2} V^{-2/3} \sigma_g, \quad \dots (3)$$

where N is Avogadro's number, and V is the molar volume. Inserting numerical values in Eq. (3) we find that $\sigma \cong 12 \text{ ergs} \cdot \text{cm}^{-2}$. When this value is substituted in Eq. (1), a temperature change $\Delta T = -177^\circ \text{C}$ results. Thus the interfacial energy between solid and liquid phases existing within the droplet serves to depress the temperature at which the solid and liquid can coexist, and according to this estimate it does so by an amount sufficient to lower the melting point below 0°C .

It should be pointed out that the expression, Eq. (1), was derived taking into account only first order terms in an expansion of free energy in terms of temperature and pressure. Inclusion of higher terms in ΔT in the present case undoubtedly would decrease the resulting magnitude of ΔT . In addition,

the treatment in terms of surface and volume properties of the bulk metal may require revision in the case of particles which contain only a small number of atoms. The large ΔT resulting from the first order calculation, however, may be taken as a fairly strong indication that colloidal potassium particles as small as 20 Å in diameter exist in a liquid state at room temperature and above.

The pressure necessary to effect the required 14-1/2 per cent reduction in volume may now be determined from another set of curves obtained by Bridgeman;^{9b} it is about $0.6 \times 10^4 \text{ kg} \cdot \text{cm}^{-2}$ at room temperature. The pressure, we have seen, due to surface tension in a 20 Å particle is about $0.8 \times 10^4 \text{ kg} \cdot \text{cm}^{-2}$. Thus it appears that the surface tension is adequate to account for the necessary reduction in particle volume for particles of this size, so that no strong interaction with the lattice need be assumed. (It is of interest to note that this volume reduction is not a factor in the photographic process in the silver halides; there is plenty of room for the compact f.c.c. silver particles.) We may mention further that the surface energy of solid potassium, according to recent theoretical^{12, 13, 14} and experimental¹⁵ results, is about equal to that of the liquid, so that we probably are safe in calculating the compression due to surface forces by using the liquid surface tension, even should the conclusion that the particles are liquid prove incorrect.

The importance of the physical state of the metallic particles in determining their optical properties suggested the value of an experiment to see if evidence could be obtained for a transformation from solid to liquid particles when the temperature of a crystal containing the particles was raised. Absorption spectra therefore were taken at intervals of about 30° at successively higher temperatures, starting at room temperature and extending to 250°, the temperature at which the colloidal dispersion in the additively-colored crystal used had previously been brought to thermal equilibrium. Some of the spectra obtained are shown in Fig. 1. It will be seen that only a uniform and gradual shift of the colloidal peak occurred, with no evidence of the discontinuity which should be expected if an array of solid particles suddenly became melted. This melting must occur somewhere below the highest temperature reached even if the influence of the solid-liquid interface is entirely negligible, and such a transition is accompanied by a sharp discontinuity in the electrical conductivity, the property chiefly responsible for the crystal's optical behavior. Since no

Fig. 1. Effect of Elevated Temperatures on the Colloidal Band

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evidence of such a discontinuity is visible in Fig. 1, it may be regarded as very probable that the particles are in the liquid state throughout this entire temperature range, and the calculations above suggest that the influence of the liquid-solid phase change should rather be found somewhere between room temperature and dry-ice temperature. Thus, unless it can be demonstrated that the particles actually are much larger than 20 Å, an assumption that there is negligible strain interaction with the lattice appears to be justified, and optical property calculations should be based on optical data for liquid metals under pressure. Certain features of the existing optical absorption calculations will be discussed briefly in the Appendix in the light of these conclusions.

III. CALCULATION OF THE HEAT OF REACTION

We return now to the reaction between colloidal particles and F-centers. Strain interaction with the KCl lattice will be neglected, but allowance will be made for a fairly high hydrostatic pressure due to surface tension.

The previous estimate⁸ was based on an indirect cycle which required use of several theoretical quantities whose values are known only approximately. It is of interest therefore to consider directly the three-phase equilibrium between bulk metal, vapor, and crystal; the heats of reaction between the phases are known from experiment. We shall find in doing so that several questions of great interest arise regarding the additive-coloring process, which experiments now in progress are designed to answer.

The condition for thermal equilibrium in the three-phase system is that the partial potentials of potassium in the three phases, defined by $\mu^{f, g, l} = \left(\frac{\partial F}{\partial n_{f, g, l}} \right)_{T, V}$ are equal. F is the free energy of the system. The partial potentials of potassium absorbed in the KCl crystal in the form of F-centers, μ^f , and in the vapor, μ^g , are given by

$$\mu^f = W_f - kT \log \frac{N^+ n_f}{n_f} - kT \log \gamma' \quad . . . (4)$$

$$\mu^g = kT \log n_v - \frac{3}{2} kT \log T - kT \log \left\{ \frac{(2\pi mk)^{3/2}}{h^3} v_o^g \right\}, \quad . . . (5)$$

where W_f is the work done in adding an atom to the crystal in the form of an F-center and γ' is a term arising from vibrational frequency changes of ions adjacent to the F-center. N , n_f are the densities of molecules and F-centers in the crystal; n_v is the density of atoms in the vapor. If the K-atom is assumed to be in a 2S state in the vapor, the electronic weight $v_o^g = 2$. Setting $\mu^f = \mu^g$ we obtain the equilibrium relation

$$\frac{n_f}{N + n_f} \cong n_v \frac{\gamma'}{2} \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} \right\}^{-1} e^{-W_f/kT} \quad . \quad . \quad . \quad (6)$$

which, since $n_f \ll N$, reduced approximately to

$$\frac{n_f}{n_v} \cong N \frac{\gamma'}{2} \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} \right\}^{-1} e^{-W_f/kT} \quad . \quad . \quad . \quad (7)$$

This expression differs from an equation derived by Mott and Gurney¹⁶ in containing explicitly the factor $\gamma'/2$, to take account of the vibration entropy of the crystal and the contribution of the electronic weight of the atomic 2S state to the partition function for the vapor. These corrections are included principally for completeness, since the value of γ' is unknown at present, but the magnitude of γ' will be estimated below from the available data and the resulting value used to check the reasonableness of this theory. The factor in curly brackets is inverted in Mott and Gurney's equation, due to an error in writing their partial potential for the vapor phase (their Eq. (17), page 144, Ref. 16; both signs in the bracket should be positive).*

Inserting numerical values for a temperature in the region of interest, 600° C, the value of $\left\{ \frac{(2\pi mkT)^{3/2}}{h^3} \right\}$ is $1 \times 10^{27} \cdot \text{cm}^{-3}$. The density of molecules N is $1.6 \times 10^{22} \cdot \text{cm}^{-3}$. Thus Eq. (6) without the negative exponent leads to an absurd result. The correct form, however, leads to a reasonable expression:

$$(n_f/n_v)_{600^\circ} \cong 10^{-5} \gamma' \exp(-W_f/kT) \quad . \quad . \quad . \quad (8)$$

An experimental determination of W_f by Rögner¹⁷ yielded the negative value $W_f = -0.10 \text{ ev}$. Combining this with Rögner's experimental value for n_f/n_v at 600°, $n_f/n_v = 1.7$, γ' may be calculated from Eq. (6). The value

*Note added in proof: The correct expression appears in the 1950 reprinting of Reference 16.

$\gamma' = 5 \times 10^4$ results. This is unreasonably high, since γ' as noted above is determined principally by frequency changes in the vibrations of ions neighboring the F-centers, and Mott and Gurney estimate less than 10^2 for the analogous factor γ (page 30, Eq. (9), Ref. 16) in the case of vacancy formation. This estimate has been supported by experiment,¹⁸ and it is probable that γ' is no larger than γ and more likely is smaller. However, we shall show presently that there is reason to suspect the figure -0.10 ev for W_f ; the correct value likely is nearer -0.5 ev. If this latter value is employed, Eq. (6) yields $\gamma' = 2 \times 10^2$, a much more acceptable figure. Thus it appears, using the most recent data available, that Eq. (6) adequately describes the reaction between K vapor and KCl.

We consider next the reaction with the third phase in the system. Rather than equating μ^1 to the partial potentials in the vapor and the crystal, we may employ the equation $p = n_v kT = p_o e^{-Q/kT}$ where Q is the heat of vaporization of potassium, so that $n_v = (p_o/kT)e^{-Q/kT}$, and

$$n_f \approx \frac{p_o N \gamma'}{2kT} \left\{ \frac{2\pi mkT}{h^3} \right\}^{-1} e^{-(Q+W_f)/kT} \quad \dots (9)$$

so long as the vapor is saturated, that is, in equilibrium with a reservoir of liquid metal. Thus it is the energy $\Delta H = (Q + W_f)$ which has been measured by Scott and Smith,³ who found that $\Delta H = 0.35$ ev at 350° C. Using 22 kg calories per mole for the cohesive energy of solid potassium¹⁹ and 0.6 kg calories per mole for the heat of fusion,²⁰ the value of Q obtained is 21.4 kg calories per mole = 0.93 ev. This combined with $W_f = -0.10$ ev predicts that $\Delta H = 0.83$ ev, rather than the smaller value given above. It is desirable therefore to reconsider the experimental W_f , -0.10 ev, obtained by Rögner, since the value of Q cannot be challenged.

In the experiments of Rögner,¹⁷ KCl crystals were additively colored in K vapor, whose pressure was determined by the temperature of a liquid phase with which the vapor was in equilibrium; the liquid was maintained at a temperature which was lower than that of the crystal and could be varied independently. The essence of a three-phase equilibrium was preserved; the vapor concentration surrounding the crystal was maintained constant at a value determined by the experimental condition of no pressure difference within the coloring vessel.

In contrast with Rogener's experiment, the recent experiments of Scott and Smith are analogous to earlier experiments of Mollwo,²¹ who employed crystals containing ultramicroscopically observable colloidal particles. In this case, the metal supply is maintained always at the same temperature as the KCl crystal being colored, but otherwise, so long as the supply of particles is not exhausted, the only differences which may arise in the two experiments are those due to the hydrostatic pressure referred to above and to small interfacial energy contributions. Neglecting these, the same value should be observed for the heat of F-center formation. Now, in their experiments, Scott and Smith³ determined the equilibrium F-center concentration at several temperatures between 300 and 450° C. Using vapor pressure charts for K,²² and the relation $p_v = n_v kT$, the values of n_v at these temperatures were calculated, together with the ratios $\alpha = n_f/n_v$. The results obtained are given in Table I.

TABLE I
RATIOS OF COLOR CENTER TO VAPOR CONCENTRATION
IN KCl-K BETWEEN 300 TO 450° C

Temperature (°C)	n_f (cm^{-3})	(mm Hg)	n_v (cm^{-3})	$\alpha = n_f/n_v$
300	1.1×10^{17}	0.3	5.1×10^{15}	21
350	1.9×10^{17}	1.3	2.0×10^{16}	10
400	2.9×10^{17}	4.2	6.0×10^{16}	4.8
450	6.4×10^{17}	11	1.6×10^{17}	4.0

The resulting values of $(\log \alpha)$ are plotted vs $10^3/T$ in Fig. 2. It is evident that the points obtained for 300, 350, and 400° C lie on a straight line, whose slope is considerably greater than that of a line drawn through the two points obtained by Rögener. The energy W_f calculated from the expression $\frac{d(\log \alpha)}{d(1/T)}$ is $-0.49 \approx -0.5$ ev. As noted above, this is more satisfactorily consistent with the calculated expression for α , Eq. (6), than the older -0.10 ev. The point obtained by Scott and Smith at 450° is higher than is expected; Rögener's values at higher temperatures deviate still farther in the direction of greater α , the

Fig. 2. Concentration Ratios in the System K-KCl

observed value of α at all temperatures, according to the early work, being greater than unity. Extrapolation of the Scott-Smith curve for low temperature predicts the value $\alpha = 0.7$ at 873°K and 0.3 at 1000°K , while Rögner's values are about 1.7 and 1.5 . These observations suggest the possibility that the process of additive coloring at higher temperatures may differ from that in the range from 300 to 400°C . This question will be considered further in Section V. The final predicted value for ΔH is $0.93 - 0.49 = 0.44 \text{ ev}$, or if allowance is made for compressive work done by surface tension, which is about 0.01 ev for a $20 \text{ \AA}$ particle, $\Delta H = 0.43 \text{ ev}$. This agreement with the empirical value 0.35 ev is fairly satisfactory and serves to remove any doubt regarding the reasonableness of the colloidal particle theory, based on energetic grounds.

IV. THE THEORETICAL VALUE FOR W_f

Before examining a recent assertion in the Russian literature that additive coloring is an irreversible process, let us consider briefly a theoretical estimate that $W_f = -0.18 \text{ ev}$, with which the value -0.5 ev is in appreciable disagreement.

The estimate, made by Gurney and Mott,²³ is based on the following cycle:

1. A negative ion is removed from the crystal, requiring work W_H^- .
2. An atom in the vapor is ionized, the work done being the ionization potential I .
3. The electron is placed in the conduction band. The work done is $-\chi$ where χ is the electron affinity of the crystal.
4. The conduction electron is trapped in the field of a negative vacancy; the work done is $-E_f$, where E_f is the thermal dissociation energy of an F-center.

5. The negative and positive ions in the vapor as a result of steps 1 and 2 are placed on the surface of the crystal to build up a new layer; the work done is $-W_L$, where W_L is the lattice energy per ion pair.*

The sum of the energies in steps 1 through 5 is W_f , that is,

$$W_f = I + W_H^- - \chi - W_f - W_L \quad . \quad . \quad . \quad (10)$$

Gurney and Mott show that

$$E_f = w + \frac{1}{2} (W_H^+ + W_H^- - W_L) \quad . \quad . \quad . \quad (11)$$

where w is the observed energy of activation in an F-center mobility experiment;²³ hence, that

$$W_f = I + \frac{1}{2} (W_H^- - W_H^+) - \frac{1}{2} W_L - \chi - w \quad . \quad . \quad . \quad (12)$$

Mott and Gurney regard all but the second term on the right as experimentally determined. It is instructive to reproduce the values obtained for the quantities appearing in W_f for several alkali halides (Table II).

It will be noted that χ , the depth of the bottom of the conduction band, is considerably smaller for KCl than for the other crystals. The value given in Table II is obtained by combining a theoretical estimate of ψ/h , the low-frequency cutoff for photoelectric emission from KCl into a vacuum, with the measured frequency of the second peak in the ultraviolet absorption spectrum. (The first peak is due to exciton transitions; the second is assumed to be a

*Calculations by J. Hove²⁴ suggest that the KCl molecule does not add to the crystal, but rather remains in the vapor phase or condenses elsewhere, due to the small interaction of molecular KCl with the KCl lattice. If this is the case, W_L should be replaced by the slightly smaller binding energy of the KCl molecule. An experiment to test this theory is planned. A KCl crystal colored in Na vapor should, according to the usual picture, contain a concentration of Na equal to the F-center density; according to the second mechanism it should contain a negligible amount of Na. The concentrations involved are easily observed by flame spectrophotometry, and such an additively-colored KCl crystal will be examined for its content of Na.

TABLE II²³
CONTRIBUTIONS TO W_f
(Energies in ev)

	NaCl	KCl	KBr
I	5.11	4.32	4.32
- χ	-0.53	-0.07	-0.70
-w	-0.94	-1.00	-0.84
$1/2(W_H^- - W_H^+)$	+0.28	+0.16	+0.19
- $1/2 W_L$	-3.97	-3.59	-3.45
W_f (calculated)	+0.05	-0.18	-0.48
W_f (observed)	-	-0.10	-0.25

series limit corresponding to ejection of an electron from the full 3p band into the conduction band. Illumination in the second peak has been observed to produce photoconductivity.) If ν_0 is the frequency of the series limit, then $h\nu_0 = \psi - \chi$.

The value of ψ employed in estimating χ is calculated²⁵ by means of a cycle in which

- A negative ion is removed from the KCl crystal
- An electron is removed from the ion
- The resulting neutral atom is replaced in the negative vacancy left in step (a).

The work done in step (a) is taken to be $W_L - 1/2 e \phi$, where W_L is the lattice energy per ion pair and ϕ is the electrostatic potential at the lattice point of the displaced ion due to the dipoles induced on the surrounding ions. That in step (b) is E , the electron affinity of the negative ion; that in step (c) is assumed to be zero. The total energy ψ then is given by

$$\psi = W_L - 1/2 e \phi + E \quad . \quad (13)$$

Values of the contributions to ψ in KCl are given in Table III, together with $h\nu_0$.

TABLE III²⁵

CONTRIBUTIONS TO ψ IN KCl

W_L	7.18
$1/2 e \phi$	1.44
E	3.75
ψ	9.49
$h\nu_0$	9.4 ₂

According to Table III, χ is a small difference between two large numbers, ψ and $h\nu_0$; and ψ itself, as we have seen, contains the theoretically-determined quantity $1/2 e \phi$. Thus χ cannot be regarded as an experimentally determined contribution to W_f ; and an error of 10 or 20 per cent in ϕ would remove the discrepancy between the theoretical and experimental values of W_f .

It is probable that the value for ϕ in Table III is in error by considerably more than this. The value given there (compare Table 19, Ref. 25, and Table 15 in the same volume) is calculated for the case of a rigid polarizable lattice; that is, one in which only electronic polarization is allowed. In their original calculation, Mott and Littleton²⁶ found that polarization of the ionic lattice about a negative vacancy in NaCl increased the energy contribution from polarization effects from $0.29 \frac{e^2}{a}$ to $0.58 \frac{e^2}{a}$ or by a factor of 2. The values for KCl are not presented in Ref. 26, but the effect of ionic polarization should be of similar magnitude. Now, this ionic polarization occurs in step (a) of our cycle, and it is not removed when the neutral atom is replaced in step (c). Thus it is incorrect in writing Table III to employ the value of ϕ calculated for the rigid lattice. Actually, the true value probably lies somewhere between 1.44 and a value about twice as large. This uncertainty of the order of 1 ev, together with the present highly unsatisfactory state of the theory of the internal field in a crystalline insulator, suggests that the foregoing calculation of χ cannot be expected to yield an accurate result.

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RE: Erratum in NAA-SR-1050, page 20

Please insert this page opposite page 20.

The quasi-static cycle used in computing ψ led to an error; it gives the correct value only if ϕ for the rigid polarizable lattice is employed, as was done by Mott and Gurney, since the physical process under consideration is an optical transition for which the Franck-Condon principle applies. Thus the discussion in the last paragraph on page 20 and the conclusion that ϕ is uncertain by 1 ev is fallacious. However there remains sufficient uncertainty in the electronic polarization calculation to permit adjustment of χ by several tenths ev.

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Conversely, the value for W_f obtained above suggests that χ in KCl actually is comparable to the values given in Table II for KBr and NaCl. The true value of χ might be obtained experimentally either directly, by measuring ψ/h , the photoelectric threshold for KCl, or indirectly, by measuring the thermionic emission from an alkali metal into the conduction band of KCl and comparing the work function so obtained with that obtained for emission into a vacuum. Meanwhile, there seems to be no reason to challenge the value $W_f = -0.5$ ev on grounds that it is in disagreement with theory.

V. REVERSIBILITY OF THE ADDITIVE COLORING PROCESS AT HIGH TEMPERATURES

One further aspect of this problem deserves attention. In a recent paper entitled "Mechanism of Additive Coloring of Alkali Halide Crystals," Shamovsky, Rybakova, and Gosteva²⁷ describe an experiment which is claimed to demonstrate that the additive coloring process is irreversible. Their results shown in Fig. 3, indicate that the concentration of F-centers formed in KCl at a given temperature is independent of the concentration of atoms in the vapor; this was claimed to be true so long as the vapor is saturated. The concentration in the vapor at a given temperature in these experiments was varied by varying the alkali metal, and thus the vapor pressure. (The ordinates in Fig. 3 evidently were mislabelled; they are incorrect for the vapor concentrations, and if they were correct for the F-center concentrations no optical determination of F-center density would have been possible.) These authors have tested the irreversibility of the coloring reaction by lowering the temperature following attainment of equilibrium at a higher temperature; it is stated that no decrease in F-center concentration was observed, although "the experimental conditions (at the lower temperature) were such that the processes were not hindered." No experimental details are given. In all cases these authors obtained a limiting F-center concentration given by

$$N_f = 3.98 \times 10^{23} e^{-23,770/kT} \text{ cm}^{-3} \quad \dots (14)$$

where T presumably is the highest temperature attained by the crystal during the coloring process.

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Fig. 3. 1, Limiting Concentration of F-centers in Sylvite Crystals in Saturated Vapors of Alkali Metals: a of Potassium, b of Sodium, c of Rubidium, and d of Cesium. The Concentration of Atoms of the Alkali Metal in Saturated Vapors (Number of Atoms Per cm³): 2 of Potassium, 3 of Sodium, 4 of Cesium, 5 of Rubidium.

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These results contradict entirely the basic assumption on which all of the foregoing theory has been predicated: that the reaction between the vapor and the crystal is an equilibrium process. If the results in Ref. 27 are correct, most of the present discussion is meaningless. It is of great importance, therefore, that these results be subjected to a further check, particularly since Ref. 27 leaves most of the significant details unknown, and the curves presented contain errors. Appropriate experiments therefore now are in progress. It should be noted that the 300, 350, and 400° C F-center concentrations obtained by Scott and Smith³ appear strongly to confirm the reversibility of the process in that temperature range. One may speculate whether the deviations at higher temperatures (all of the Russian work was done above 450° C) are due to unknown experimental conditions or do indeed reflect a basic change in the nature of the additive coloring process. Rögner's results provide no answer to this question, and the current experiments are being carried on both above and below 450° C in order to provide a basis for decision.

The explanation for the observed irreversibility which is advanced in Ref. 27 depends on an assumption that negative ion vacancies are formed by the Frenkel process, rather than by Schottky's mechanism. Employing the energy level diagram shown in Fig. 4, it is asserted that if

$$\phi_o - \phi - W_f < kT \quad . . . (15)$$

(ϕ is our χ , above; ϕ_o is the metal's work function; E_f is the same as above) or if $\phi_o - \phi < E_f$, then electrons will enter the crystal through the conduction band by thermionic emission, filling all of the available vacancies (if our conjectures above regarding χ are correct, then $\phi_o - \phi < E_f$). The removal of a corresponding number of anions then takes place by migration of the interstitial anions, aided by a space-charge-induced potential gradient at the metal-crystal interface. The expression (Eq. (14)) is interpreted as giving the equilibrium concentration of anionic Frenkel defects, and this concentration is assumed to remain unaltered by the process of coloring even though electrons are trapped in the negative vacancies.

This picture is unsatisfactory for a number of reasons. First, the calculations of Mott and Littleton²⁶ supposedly rule out the possibility of Frenkel defects for energetic reasons. Second, it is not clear, even if the process of electron trapping in anion vacancies were irreversible, why the process of lattice defect formation should be reversible until the crystal is colored (so

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Fig. 4. Energy Levels in the System K-KCl

that the vacancy concentration is described by the equilibrium expression above) and irreversible after the coloring is started (so that no more vacancies are formed to replace those which trap electrons). Third, the explanation of Rögner's contradictory results, in which the vapor concentration obviously did affect the concentration in the crystal, is based on an idea that his experiment was done with non-saturated vapor, and that the thermionic work function of an adsorbed layer of alkali metal on the crystal was varied thereby. While this problem deserves further attention, it may be immediately observed, as noted above, that Rögner's experiment did involve a saturated vapor. Although the vapor was in equilibrium with a reservoir of metal at a lower temperature than that of the crystal, its concentration was maintained constant in spite of absorption in the crystal. In addition, an estimate can quickly be made which

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suggests that no appreciable adsorbed layer is formed during the coloring process, even in the saturated vapor. The adsorbed potassium may be treated by the methods appropriate to the problem of the regular localized monolayer,²⁸ although it is not certain that the K-KCl interaction is strong enough to justify this treatment; on the other hand, if it is not and the K is mobile on the crystal surface the conclusion below follows even more certainly. This calculation yields the well-known Langmuir adsorption isotherm

$$\frac{\theta}{1 - \theta} = \frac{p}{p^*} \quad , \quad \dots (16)$$

which has limiting forms

$$\theta = \frac{p}{p^*} \quad (p \ll p^*) \quad \dots (17a)$$

$$\theta = 1 \quad (p \gg p^*) \quad \dots (17b)$$

In these expressions θ is the fraction of available sites occupied by adsorbed K; p is in this case the pressure of the potassium vapor, and p^* is a "vapor pressure" for the adsorbed layer. If it is assumed that the three translational degrees of freedom of an adsorbed K atom in the monolayer are classical harmonic oscillations of mean frequency ν , their contribution to the partition function is $(\frac{kT}{h\nu})^3$, and the pressure p^* is approximately given by

$$p^* = (2\pi m)^{3/2} \nu^3 (kT)^{-1/2} e^{-Q_m/kT} \quad , \quad \dots (18)$$

where Q_m is the depth of the potential of K in the monolayer, including interactions with other adsorbed K. The comparison between p and p^* is equivalent to comparing the numbers n , n^* of atoms striking and leaving the surface per unit time, since in general p and n are related by

$$n = \frac{p}{(2\pi mkT)^{1/2}} \quad \dots (19)$$

At 600° the pressure of K vapor is about 200 mm; this gives $n = 3.8 \times 10^{22}$ atoms·cm⁻²·sec⁻¹. The corresponding value of n^* depends on the value assumed for ν . An estimate by J. Hove²⁴ for the case of ionized K on KCl leads to a value of about 10^{12} sec⁻¹. If the value of ν in the case of unionized

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K is less than about 10^{11} the localized monolayer concept no longer applies, but the binding then probably is so small that no layer of any density is formed, so we shall take 10^{12} as an upper and 10^{11} as a lower limit for ν . Taking the larger value we find

$$n^* = 3.4 \times 10^{27} e^{-Q_m/kT},$$

while the smaller reduces this expression by the factor 10^{-3} .

Now, the condition for the formation of an appreciable metallic phase on the crystal surface is $n = n^*$; for $n < n^*$ no layer is formed, while for $n > n^*$ a metallic phase is built up rapidly. Thus we may equate n and n^* , and from the foregoing expressions calculate the necessary magnitude of Q_m for the formation of an adsorbed layer to occur. This calculation for the case $\nu = 10^{12} \text{ sec}^{-1}$ yields $Q_m = 0.86 \text{ ev}$; for $\nu = 10^{11} \text{ sec}^{-1}$, $Q_m = 0.35 \text{ ev}$. In other words, if the K atom is less tightly bound on the KCl surface than by a potential amounting to -0.35 ev , it is probable that no appreciable adsorbed layer is formed at 600° C . A value of 0.3 ev has been calculated by Hove²⁴ for the binding energy of molecular KCl on crystalline KCl. The value for K on KCl should be somewhat smaller. Thus it is by no means certain that a metallic layer is formed on the crystal surface during additive coloring; rather, it is highly probable that such a formation does not occur. We conclude, therefore, that the interpretation of Rögner's experiments in terms of a non-saturated vapor and the thermionic properties of an adsorbed layer must be incorrect.

Finally, we may note that the theory developed in the previous sections suggests that similar F-center concentrations should be obtained when KCl is heated in the vapors of a variety of alkali metals, in agreement with the observation in Ref. 27. Let us consider KCl colored by Na and by K for example. If the ratio given by Eq. (6) for n_f/n_v in the system K-KCl is α , then according to Eq. (6) the ratio for the system Na-KCl should be given by

$$\frac{n_f}{n_v}(\text{Na-KCl}) = (\alpha) \left(\frac{\gamma'_{\text{Na}}}{\gamma'_{\text{K}}} \right) \left(\frac{m_{\text{K}}}{m_{\text{Na}}} \right)^{3/2} e^{-(W_f^{\text{Na-KCl}} - W_f^{\text{K-KCl}})/kT} \quad \dots (20)$$

Referring to Table II, we note that W_f will be larger in the system Na-KCl by the difference in ionization potentials of Na and K, or 0.8 ev. If this were the only difference in W_f in the two cases, the F-center concentration at 700° C, for example, in Na-KCl would be a factor of 10^{-4} smaller than that in K-KCl at that temperature. That is, the crystal would hardly be colored at all by Na vapor at 700° C. A contribution to W_f in the opposite sense results, however, from the decreased repulsion interaction of Na in the KCl lattice. A lower bound for the magnitude of this effect may quickly be estimated if it is assumed that no relaxation of the lattice occurs in the vicinity of the Na^+ impurity ion (relaxation of course does occur, with accompanying polarization effects, but all of these effects decrease still further the total energy of the system so we are in fact calculating a lower limit here). Using the basic ionic radii listed by Mott and Gurney, the repulsion energy of K^+ in KCl is 1.5 ev, considering only nearest-neighbor interactions, while that of Na^+ in a rigid KCl lattice is only 0.6 ev. The difference, 0.9 ev, is opposite in its affect on W_f to that of the 0.8 ev difference in ionization potentials of Na and K. Thus it would appear that W_f is approximately the same in both systems (and also probably in systems such as Rb-KCl, where a larger repulsion is counteracted by a smaller ionization potential). The exponential term therefore is relatively unimportant; the concentrations are determined mainly by the entropy factors γ'_{Na} , γ'_{K} . Vibrational frequency changes occur adjacent to a Na^+ ion in KCl which have the effect of increasing γ'_{Na} , relative to γ'_{K} , which includes only effects due to the F-center itself; the increase in γ counteracting the decrease in atomic concentration in the vapor (the latter decreases by about a factor of 5 in going from K to Na at 700° C). It is not suprising, therefore, or in disagreement with the equilibrium theory we have developed, that comparable F-center concentrations occur in crystals of KCl colored in a variety of alkali metals. This observation thus is not valid evidence of irreversibility in the coloring process.

The fact that lowering the temperature did not shift the equilibrium toward a lower concentration is evidence for irreversibility, however. On the other hand, Rögener's experiments, which showed that the F-center concentration in the system K-KCl did depend on vapor pressure, and the results obtained at lower temperatures by Scott and Smith, are evidence for a reversible coloring reaction. Thus we are left with conflicting experimental

results, a decision between which demands recourse to further experiments. As noted above, we are at present undertaking such experiments, with a three-fold objective: (1) to test the reversibility of the additive coloring reaction and distinguish between fundamentally different processes in the temperature ranges below and above 400°C if they exist, (2) to determine W_f in both regions, and (3) to distinguish between the usually assumed coloring mechanism in which the crystal gains atoms from the vapor, and the process predicted by Hove, in which K from the vapor combines with Cl^- on the surface of the crystal, with re-evaporation of the KCl molecule so formed. It cannot yet be stated with assurance whether or not the coloring process differs in the two regions of temperature. The lower region corresponds roughly to the non-equilibrium, or structure-sensitive region of various transport phenomena, where the lattice defect concentration is determined by impurities and thermal or mechanical history; this mainly is the region in which radiation-damage annealing processes have been studied.⁷ On the other hand, transport phenomena at higher temperatures generally involve equilibrium behavior. One might anticipate, therefore, different coloring processes in the two ranges of temperature, but normally the higher temperatures should lead to reversibility and equilibrium behavior, whereas the reverse actually seems to be the case. It is hoped that the present experiments will resolve this apparently anomalous situation.

In addition to the experiments mentioned above, an effort is being made to arrange for the measurement of the photoelectric threshold for KCl in order to have an experimental value for ψ . The result of this experiment should be of value in that it will indicate the degree of accuracy of the presently available calculations of polarization effects in the alkali halide lattice, which form the basis for all of the present calculations of the lattice-defect energy in these crystals.

VI. CONCLUSION

The apparent disagreement between predicted and experimental values for the heat of reaction between colloids and F-centers, $\Delta H = Q + W_f$, has been shown to be largely eliminated if W_f is calculated from the most recent experimental data, that of Scott and Smith. The value for W_f thus obtained

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has been compared with theory, and the discrepancy shown to be due most probably to inaccurate knowledge of χ , the electron affinity of KCl. It has been demonstrated that the new value of W_f leads to a quantitatively reasonable prediction of the color center concentration in KCl as a function of vapor pressure during the coloring process, whether the liquid metal reservoir is within or outside of the crystal. An apparent deviation of the coloring process from reversibility at high temperatures is discussed, and current experiments are described which will provide the information required before the mechanism of coloring can be definitely established. It has been shown finally that colloidal particles of metal embedded in the KCl crystal most probably are in liquid form, under a high hydrostatic pressure resulting from surface tension, and that current interpretations of the optical absorption properties of colloiddally-colored crystals require modification to take this effect into account. A future report will describe a study of the kinetics of the color-center coagulation reaction, in terms of a two-step process.¹ In the first step, which is greatly accelerated by light, the color centers are destroyed; in the second, the resulting intermediate centers (Zwischenzentren) become aggregated into the colloidal particles whose thermal properties it has been the purpose of this report to discuss.

NOTE ADDED IN PROOF: Several developments since this was written in early 1954 deserve mention. The problem of ΔH has been considered also by Seitz, Rev. Mod. Phys. 26, 1 (1954) and by Scott, Phil. Mag. 45, 610 (1954), the latter concluding that interfacial energy between crystal and particle, which was assumed negligible in this report, serves to sufficiently depress ΔH . The apparent W_f in the low-temperature region in this case would be lowered by the amount of the interfacial energy. The correctness of this conclusion will be known when a definitive experiment determining W_f in the high-temperature region, where particles do not exist, is completed.

An experiment appearing to confirm reversibility in the temperature range 5-600° has been completed D. R. Westervelt, Bull. Am. Phys. Soc. 29, No. 6, 9 (1954).

A revised estimate of the effect due to surface tension has been completed, taking into account the fact that atoms removed from the metal particles' surface by the normal surface tension process must be accommodated in the interior. Therefore there are volume as well as surface contributions to the free-energy change and the usual free-energy calculation must be modified in determining the effective surface tension. The total free energy was calculated as a function of surface area (or volume compression), assuming the surface layer to be undistorted, for a wide range of initial particle sizes. For the entire range of particle sizes of interest (10-100 Å°) the energy minimum occurred at a volume compression of about 6%. Thus the required 14% decrease apparently does not occur due to this effect alone as concluded above, and vacancy pairs probably contribute to the stress-relaxation as suggested by Seitz and Scott.

APPENDIX

OPTICAL PROPERTIES OF A COLLOIDAL DISPERSION

In their treatment of the optical properties of colloidal alkali metal in alkali halides, Scott, Smith, and Thompson³ have employed an equation derived by Pohl²⁹ for the extinction coefficient K :

$$K = \frac{36\pi N_v V}{\lambda} \frac{nk/n_u}{4 \left[1 + \left(\frac{n}{n_u} \right)^2 - \left(\frac{k}{n_u} \right)^2 \right] + \left[\left(\frac{n}{n_u} \right)^2 + \left(\frac{k}{n_u} \right)^2 \right]^2} \quad \dots (A-1)$$

where the product $N_v V$ gives the volume of colloidal material per unit volume, λ is the wave length in air, n and k are defined by $m = n - ik$, where m is the complex refractive index of the alkali metal, and n_u is the refractive index of the alkali halide. Since $n \ll k$, the wave length of the absorption peak is determined approximately by the condition $k = \sqrt{2n_u}$, for which the denominator goes to zero. Using the extrapolated optical data of Ives and Briggs³⁰ for solid bulk potassium, Scott, Smith, and Thompson obtain the theoretical value $730 \text{ m}\mu$ for the peak in K-KCl, for the smallest particles. Their experiments, on the other hand, give $775 \text{ m}\mu$ for the peak location.

It is worth noting that the procedure used in deriving Eq. (A-1) is incorrect; moreover, that Eq. (A-1) makes no provision for the dependence of peak wave length upon particle size. Pohl's derivation consists of a calculation of the dielectric constant ϵ of a dispersion of metal spheres, followed by a "two-fold application of the Maxwellian relationship", i. e., $n^2 = \epsilon$. Pohl's Eq. (219),

$$n_L^2 = n_u^2 + 3N_v V n_u^2 \frac{\left(\frac{n}{n_u} \right)^2 - 1}{\left(\frac{n}{n_u} \right)^2 + 2},$$

where L refers to a "solution" of particles of index n in the medium n_u , is derived from a correct equation for the dielectric constant, namely

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$$\epsilon_L = \epsilon_u + 3N_v V \epsilon_u \frac{\frac{\epsilon}{\epsilon_u} - 1}{\frac{\epsilon}{\epsilon_u} + 2},$$

by substituting n_u^2 for ϵ_u , n_L^2 for ϵ_L , and n^2 for ϵ , for the case of non-absorbing particles. Then the equation is "expanded to the case of adsorbing particles," by replacing n_L by $(n_L - ik_L)$, n by $(n - ik)$, and so forth, the final absorption coefficient being the imaginary part of the expression which results. But this procedure is incorrect; the correct substitution in each case is $\epsilon = (n^2 - k^2)$, not $(n - ik)^2$. When this substitution is made, one obtains the correct form of Pohl's Eq. (219), namely,

$$n_L^2 - k_L^2 = n_u^2 + 3n_v V n_u^2 \frac{(n^2 - k^2) - n_u^2}{(n^2 - k^2) + 2n_u^2},$$

assuming $k_u \cong 0$. This equation clearly affords no method of calculating k_L without further information, since both n_L and k_L are unknown. The correct procedure is to employ the scattering theory derived by Mie² and applied by Savostianowa³¹ to the case of Na particles in NaCl. The Mie theory reduces to Eq. (A-1) for very small particles, the extinction here being due purely to absorption, but contains additional terms for larger particles which give rise to a shift in the peak wave length. Discrepancies still appear to exist between the observed spectra and the predictions of the correct Mie theory, and this problem is receiving additional attention. In particular, the conclusion mentioned above that the particles are in liquid form under high pressure makes the use of bulk metal optical properties in calculating the band width and peak location very questionable.

In addition, some explanation is desired for the shift of the colloidal peak to longer wave lengths upon cooling to liquid-nitrogen temperature, which was described recently,³² and for the extraordinary sharpness of the "colloidal" peak in well-annealed crystals. The present considerations do not necessarily argue against the colloidal particle theory; they merely show that its present application requires certain modifications before the situation may be regarded as entirely satisfactory. It is to be hoped that a low-angle X-ray study of the colloidal particle size, which is planned for the future, combined with more appropriate metallic refractive index data, will adequately explain the

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apparently curious optical phenomena which have been observed and contribute to a more complete understanding of the process of lattice defect coagulation in the alkali halides, and in other crystalline systems whose properties depend on the nucleation and growth of metallic particles.

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