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April 1966

National Aeronautics and Space Administration

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The reports that follow comprise the various project results during the period from 7/13/65 to 1/31/66 from the research supported under the grant NsG-394 Supplement 2. In addition, the various activities (not of specific project-type research) reported initially in the February 1965 semi-annual report have continued.

The reports within a multidisciplinary research area are grouped together in the same order as in the initial research proposal of February 1965 in order to facilitate review. Several reports either announce a forthcoming talk which is already scheduled to be presented at a conference or are accompanied by a paper which is to be submitted for publication, all of which is based on the work during this period.

It is expected that several other projects will have papers ready for publication during the coming period, in particular, those projects involved in the research on the deHaas-van Alphen effect and the research on the effects of low temperatures and magnetic fields on biological tissue. In addition, at least one report is in preparation and will be submitted during the next 6 months as an Adelphi University report. Although these are future publications the results to be used in these reports will be based on the research conducted primarily during this period.

TITLE: The DeHaas-van Alphen Effect in Beryllium
by Dr. Richard W. Genberg

The deHaas-van Alphen (DHVA) effect is the oscillatory behavior of the diamagnetic susceptibility in metals at low temperatures. The detection apparatus for the DHVA effect consists of a null-deflection torsion balance[1] and it has been completely assembled. Calibration of the torsion balance has been conducted using a single crystal of bismuth, and at maximum sensitivity excellent resolution has been achieved since a torque of 0.001 dyne-cm. can be readily resolved.

Since the magnetic susceptibility is proportional to sin(W/H), the signals can be more easily analyzed if the magnetic field varies inversely in the time. Such a field variation produces signals of constant frequency, permitting the use of filtering techniques in order to separate the various components or frequencies. Once separated the individual components can be readily analyzed. For this reason a curve follower is being programmed the output of which will drive the field appropriately. We have been moderately successful with the field drive thus far.

Unfortunately, the high purity beryllium stock at Nuclear Metals, Inc., has been confiscated by the A.E.C. Since this is the only high purity stock (RRR $\cong$ 1,000)* of which we are aware, we shall plead with Oak Ridge for a few specimens. In the interim we shall investigate the DHVA effect in other materials including titanium.

It should be mentioned however that the specimens of titanium presently available are not of ultrahigh purity and this may prevent us from observing the DHVA effect. We shall pursue the matter until a decision can be made.

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[1] NASA Grant, NsG-394, Feb. 1965

*residual resistance ratio

TITLE: Effects of Irradiation on Thallium Substitutionally Deposited in KCl:Tl) by Dr. Anthony Lemos

The attached manuscript is to be submitted for publication (probably in the Physical Review) some time in April, 1966. It represents in part the work which has been done during the past year. The paper is still in rough draft form and hence there may be certain typographical errors and minor omissions. In brief, the paper is concerned with obtaining a rigorous formulation of the optical absorption and emission phenomena associated with deep electronic traps in the alkali halides. Of primary concern is the determination of the number of phonons stored in the lattice as a result of electronic transitions, the Huang-Rhys factors (which are a measure of the phonon broadening of the optical absorption and emission bands) and the Stokes Shift. General forms for these terms are developed Finally numerical calculations are made for the F-center. The results show reasonable agreement with experiment.

The attached manuscript appears in the Appendix.

TITLE: X-ray Studies of Radiation in Crystals by Dr. Alfred Zajac

The multiple anomalous transmission of x-rays (the multiple Borrmann effect) through perfect crystals can be treated theoretically by evaluating the normal modes of propagation of the electromagnetic wave field in the crystal. (The illustration of the method has been presented for the two field case in germanium by E. J. Saccocio and A. Zajac, "On the Proper Modes of Propagation of X-rays", Acta Cryst. 18, 478 (1965). The three field case has been treated by E. J. Saccocio and A. Zajac, "Simultaneous Diffraction of X-rays and the Borrmann Effect", Phys. Rev. 139, A255 (1965). The four field case has been solved by Chiu Ng, M.S. Thesis, Pol. Inst. of Brooklyn, N.Y.(1964).

The results obtained in the three and four field cases in germanium were studied. In particular it was found that only certain modes are anomalously transmitted. The influence of the form of polarization of the incident beam on the tramsmission of the various modes was investigated. Results of experiments on the anomalous transmission of x-rays in the three and four field cases in germanium were obtained. In these experiments the incident x-ray beam was monochromatized and polarized by anomalously diffracting it through another perfect germanium crystal.

The methods of obtaining the normal modes of propagation of the electromagnetic wave field in less symmetric crystals, such as calcite, were investigated also.

A report will be submitted in June which will be suitable for publication as a NASA Technical Note.

TITLE: Plasma Characteristics by Dr. Terry Morrone

Work has started on programming a digital computer in Fortran for solving the Boltzmann equation for a plasma. With the inputs to this first program being a set of collision cross sections for a gas plus a value of the effective electric field, the output is the electron velocity distribution function. More complicated problems involving Coulomb collisions and optically produced plasmas will be attacked later on.

Preliminary theoretical work includes the effect of plasma oscillations. We are approaching the problem from the point of view of Dawson and Oberman[1]. They compute the conductivity for a fully ionized plasma from the Vlasov equation and find that plasma waves are excited when the applied field frequency is near the plasma frequency. We are applying their method to a partially ionized plasma. This involves expanding the velocity dependence of the terms in the linearized Vlasov equation in Legendre polynomials and the time dependence in a Fourier series.

On the experimental side, a mercury discharge chamber has been constructed and tested. It pumps down well but because of outgassing and small leaks it cannot keep mercury at one micron pressure from being contaminated with air. We are constructing a continuous feed system and we may have to put in a "keep alive" electrode.

A two wire microwave transmission line for use in a plasma has been tested. The power transmitted is about 20 db less than the incident power. We are working on matching sections to decrease the transmission loss.

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[1] Dawson, J. and Oberman, C., Physics of Fluids, Vol. 5 517 (1962).

TITLE: Analysis of Biological and Ecological Systems in Non-equilibrated Environments - by Dr. Harry Brenowitz and Dr. Ronald Wilson

The study of complex interrelationships between the endemic populations of a disturbed ecosystem have been continued and extended to specific flow patterns of the dominant species populations at the various trophic levels within the system. In general, the latest work indicates that a disturbed system can be dominated by a primary producer which blocks energy flow to higher trophic levels causing the system to fail. The following laboratory experiments have been undertaken.

I. The Utilization of the Marine Algal Form Nannochloris in the Nutrition of the Clam.

Experiments have been performed using radioactive $C^{14}O_2$ to tag carbon transferred from CO_2 taken up in photosynthesis by Nannochloris to clams grown in pure cultures of this alga. If C^{14} uptake in the clam can be demonstrated by obtaining higher than background radiation counts when various tissues of the clam are analyzed, it is likely that the clam can utilize Nannochloris in its nutrition.

Three experimental groups were set up:

A. Clams grown in pure culture of tagged Nannochloris
B. (Control 1) Clams grown in non-tagged Nannochloris pure culture.
C. (Control 2) Clams grown in Nannochloris-free environment but with $C^{14}O_2$ in medium

Length of Time Exposed to Media (Hrs.)

	8			16			30			$83\frac{1}{2}$		
Exp. group	A	B	C	A	B	C	A	B	C	A	B	C
Tissue anal												
entire clam	441	480	523	412	406	434	447	464	391	446	401	410
gills	545	430	472	407	439	422	444	390	361	450	394	409
adduct.musc.	461	450	470	427	465	385	503	422	369	376	416	408
foot musc.	396	427	447	467	401	401	476	478	400	395	386	370

Background counts averaged 397

The first experiments have provided the above data, which would seem to indicate that the clam does not use Nannochloris as a food source. Similar experiments are being performed with

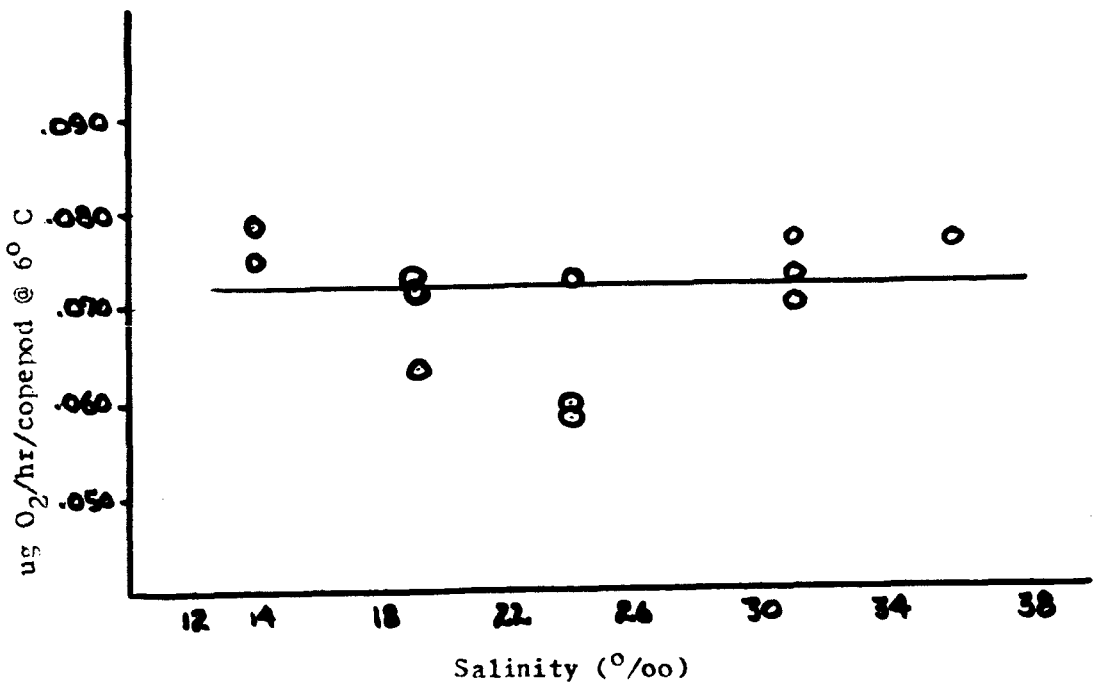
the bay scallop. Preliminary results would seem to indicate that like the clam, the scallop cannot utilize Nannochloris.

II. The Utilization of the Marine Algae Form Nannochloris in the Nutrition of Zooplankton.

Preliminary results indicate that the copepods, the chief component of the primary consumers amongst the Zooplankton do not utilize Nannochloris.

III. Respiration of Esturine Copepods as a Function of Salinity.

A study has been conducted to determine the effect of salinity on the respiration of neritic copepods. Copepods were freshly collected from estuarine waters and adapted to various salinities in the laboratory. Using a microtitration modification of the Winkler method for oxygen determination oxygen consumption of small selected groups of copepods (25-35 animals) was measured over a 24 hour period at salinities from 14°/oo to 36°/oo. Preliminary analysis of data indicates that salinity has no significant influence upon the respiratory mechanism of copepods. This supports the suggestion that the osmoregulatory mechanisms of euryhaline microcrustacea consists of energy rich electron transfer systems, demanding very small fractions of the total metabolic energy. Further analysis of data is presently being carried out.



Each point represents the average of 10-30 trials. Mean copepod cephalothorax length per trial ranges from .92 to .97 mm.

IV. Test of Methods to Determine the Relative Fishing Efficiencies of Three Different Size Plankton Nets. Three size nets 6", 12" and 20" diameter openin s are being used.

To date one complete series of samples were taken. The results based on the one series indicates a close correlation between the 12" and 20" nets for 9 of 10 key species counted. The 6" net had a correlation based on 3 of the 10 key species. Further tests are planned in order to determine the most accurate way to decide the planktonic population.

Number of Organisms/Liter of Sea Water According To:

Type Cell	6" Net	12" Net	20" Net
1. Thallassiothrix	2,152	5,200	2,750
2. Asterionella	39,150	93,930	98,930
3. Skeletonema	222,000	1,040,290	1,059,220
4. Chaetoceros	2,460	6,425	4,450
5. Nitzchia	8,712	8,875	11,230
6. Rhizosolenia	920	1,225	1,060
7. Silicaflagellate	307	1,377	1,275
8. Navicula	410	1,530	1,485
9. Coscinodisc	205	-0-	210
10. All Cells	457,540	1,223,865	1,313,430

In August and September 1965, the "small forms", mainly Nannochloris which had previously been insignificant in numbers suddenly bloomed in several areas of the bay. Organisms in excess of 9.7×10^6/ml. were found at some of the stations sampled. In addition to the experiments described previously, additional work to determine the cause of a bloom of such proportions is being planned. The preliminary data seems to bear out the idea the primary producer, Nannochloris can and does block energy flow to the higher trophic levels.

TITLE: The Effects of Some Physical Parameters on Biological Materials by Dr. Ronald Gillespie

This research is concerned with a study of the optimum rates for supercooling and thawing of living tissue, the effects of temperature changes on electrolyte constitution, and the effects of strong magnetic fields on living tissue. More explicitly these studies are on small animals and fall into three main areas.

1. Survival from supercooled temperatures
   a. by use of antifreeze agents alone and in combination
   b. by varying the rates of cooling and rewarming
   c. by use of animals of different ages

2. Changes in tissue electrolytes at different temperatures

3. Effects of magnetic flux and ionizing radiation alone and in combination

Results up to the present indicate that survival from low temperatures is appreciably increased by use of antifreeze agents and faster cooling rates. The effect of age on survival is not as pronounced, although there are some indications that younger animals survive better than older ones. Further studies with methods to increase the survival rates of small animals from temperatures below $0^{o}C$ are being conducted. Changes in the pH and electrolyte components at different cooling rates are being measured and methods of correcting these as they occur are being tried. Different rates of rewarming by using a recently obtained diathermy apparatus are also being investigated. Some of these studies are done on whole animals and others on isolated organ perfusates. Better control of the environment is possible by the latter method and the data obtained is used in the experiments involving whole animals. Quantitative results will be available soon.

Preliminary studies with rabbits have shown that lowered temperatures cause alterations in the electrolyte shifts between the cells and their environment. There is some evidence that the rate of potassium transfer is altered as the temperature changes. This effect is influenced by addition of antifreeze substances. These experiments are being expanded and better sampling techniques are being developed.

Experiments with magnetic flux and ionizing radiation are being further investigated with a larger magnet with higher fields and wider pole face separation. This permits larger numbers of animals to be tested at the same time.

Studies are also being conducted on the changes in the blood parameters in relation to ionizing radiation, magnetic flux, pressure, and temperature changes. The effects of these forces are being tried alone and in various combinations. Apart from assessing the changes which might occur to this system in space travel, the possibility of altering the leucocyte count without damaging the organism might prevent the antibody antigen reactions involved with whole organ transplants.

TITLE: Synthesis and Physical, Chemical Properties of New Metal Acetylacetonates Polymers by Dr. Alfred Vogel

The goal of the research work is to prepare a metal chelate of 2,4-pentanedione which has a halogen, preferably bromine, substituted in the one position. It is expected that the bromine in the chelated product of 1-Br-2,4-pentanedione will not lose its functional group character and thus will undergo a reaction such as a Grignard which could lead to formation of a carboxyl group on the chelate molecule. This can then serve as a site for polymerization with diols to form metal-containing organic polymers.

The literature reports no 1-substituted halogen pentanedione metal chelates (except 1-fluors chelates which do not undergo reactions at the fluoro group). Various workers have prepared metal chelates of 3-bromo-2,4-pentanedione, but the bromine in this position is not a reactive functional group, probably due to the aromatic character of the ring it occupies in the chelated structure.

1-Bromo-2,4-pentanedione has been prepared by adaptation of two different methods, and in each case, the reaction with aqueous copper acetate solution has produced a water-insoluble chelated material which is soluble in organic solvents and has a decomposition point at 139-140°C. Analysis showed the presence of three bromine atoms in the molecule. In order to ascertain the structure of this chelate, it has been compared in several ways with known chelates. Its melting point at 139°C is not the same as that of the 3-bromo-2,4-pentanedione Cu chelate (decomposes 180-200°C).

Infra-red spectra on chelated pentanedione show absorption bands at 1580 reciprocal centimeters corresponding to the perturbed carbonyl bonded to the metal. If there is a bromine in the 3-position, the band is shifted to 1552 recip. cm. Infra-red spectra have been run on (1) copper 2, 4-pentanedionate, (2) copper 3-bromo-2,4-pentanedionate and (3) our product copper 2,4-pentanedionate containing three bromine atoms.

Examination of the spectra obtained shows that (1) and (3) both absorb at 1580 recip. cm., while the known 3-bromo chelate absorbs at 1555 recip. cm. The conclusion is then that the bromine atoms introduced in the product we have are not in the 3-position. The bromine atoms must be situated on the terminal methyl groups in the molecule.

An attempt has been made to react this copper chelate with magnesium in diethyl ether to produce a Grignard reagent. No reaction occurred. Tetrahydrofuran will be substituted for diethyl ether as the solvent in the next attempt, as the higher-boiling ethers will induce reluctant halides to react with magnesium and give a Grignard reagent.

TITLE: Physical-Chemical Properties of New Silicone Polymers
by Dr. Frederick Bettelheim

The purpose of the project is to synthesize new silicones containing triazine rings as the crosslinking point of the three dimensional array and to study the mechanical-optical properties.

The synthetic part is achieved in two routes;

a) Preparing block polymers of silicones with side chains of $-CH_3$, $-C_6H_5$, $-C_6H_4Cl$, $-C_6H_3Cl_2$ and copolymerizing these blocks into linear polymers of varied compositions.

b) Crosslinking linear silicones with cyanuric chloride.

In part (a), a whole series of block polymers were synthesized. Infra-red spectra and molecular weight determination were run. The block polymers usually are of tetramers, while the simple hydrolysis products dimers.

The copolymers of the blocks usually yielded linear polymers with a degree of polymerization of 8-10. Infra-red spectra confirmed the incorporation of blocks in the designed fashion Some of these polymers yielded two phase products (i.e. one phase which was richer in methyl blocks hence being oily, another which was richer in the phenyl and chlorophenyl blocks and being solid at room temperature).

In part (b), the first success was achieved in crosslinking dimethyl-siloxanes of small molecular weights (diol to tetramers) with cyanuric chloride. The technique in essence is an interfacial condensation - the details of which will be reported at the International Symposium of Macromolecular Chemistry in Tokyo, Japan on September 28, 1966 if the travel allowance is granted. (See attached abstract).

The product is a three-dimensional network which does not decompose until 600°C and Si, N and infra-red analysis indicates an average of 2.5 crosslinks per triazine ring. Improvement of the polycondensation is now in progress also trying to incorporate silicones of longer degrees of polymerization.

Swelling properties of these new polysiloxane-s-triazinyl ethers are now under investigation

ABSTRACT

(Paper to be given at Tokyo by Dr. Frederick Bettelheim)

Dimethyl-, diphenyl-, bis(p-chlorophenyl)- and bis(3,4-dichlorophenl)- siloxanes and copolymers and block copolymers of the above were prepared with varying degrees of polymerizations. These siloxanes were condensed with cyanuric chloride under a variety of conditions. The polysiloxane-s-triazinyl ethers were characterized by elementary analysis, X-ray diffraction, IR spectroscopy Their molecular weights and solvent-solute interaction parameters were obtained by dynamic osmometer.

APPENDIX

Electron Trapping as A Function of Normal Modes

1. Introduction

Within the framework of the "adiabatic-harmonic" approximation there exists a unique set of normal lattice coordinates corresponding to each bound F-center electron state. These various sets of normal coordinates are related to one another by means of unitary transformations. The transformation matrices are dependent on the lattice equilibrium configurations which in turn are functions of the F-center electron state.

In the first portion of this paper, the matrices defining the transformation between two different sets of normal coordinates is developed. The unitary properties are then established. From these results it can be seen that, given a set of normal coordinates corresponding to a particular F-center state, one may generate the spectrum of different sets by successive applications of unitary transformations. Thus the ground state normal modes can be used as a basis set.

In the 2nd part of this article, these matrices are used to express the electron trapping energy[1] for any bound state F-center transition in terms of phonon eigenfrequencies and a basis set of normal coordinates. This formulation of the trapping energies includes degenerate and non degenerate modes and does not require the solution of Feynman-Hellman[2,3] integrals. This is in contrast to previous work.[1]

As a result of F-center electron bound state transitions, phonons are stored in the various lattice modes. From the trapping energy the number of phonons stored in the various lattice modes is determined. We consider only Frank-Condon Transitions. General expressions are then developed for the Huang-Rhys factors in terms of the stored phonons. It is shown that only under very restrictive condition are they equal.

In the 3rd part of the paper explicit calculations are carried out for the tight binding model of the F-center, where O_h and D_{4h} symmetry have been associated with those bound states giving rise to the F-band. The numerical results for the number of stored phonons, Huang-Rhys factors, and the Stokes Shift of the F-bands for several alkali halides are calculated and indicate approximate agreement with experiment.

II. Transformation Between Sets Of Normal Coordinates

Assume there exists a spacial distribution of N-ions coupled to each other in such a way that they make small oscillations about a given equilibrium configuration. We define a 3N-dimensional normalized displacement vector $\underset{\sim}{X}$, having 3N components. For convenience by $\underset{\sim}{X}_o$ (o). The ground state 3N dimensional normal coordinate vector is related to $\underset{\sim}{X}$ by the following transformation[4]

$$\underset{\sim}{q}(o) = A\ (o) \left(\underset{\sim}{X} - \underset{\sim}{X}_o(o)\right) \qquad (1)$$

The inverse transformation is

$$\underset{\sim}{X} = A^{+}(o)\,\underset{\sim}{q}(0) + \underset{\sim}{X}_{o}(o) \tag{2}$$

such that

$$A(o)\,A^{+}(o) = II \tag{3}$$

where A^{+} is the adjoint of the matrix Z and II is the identity matrix. In a similar fashion we may obtain the transformation between $\underset{\sim}{X}$ and $\underset{\sim}{q}$ (n), the normal coordinate vector associated with the electron state n. The relationship is

$$\underset{\sim}{q}(n) = A(n)\left[(\underset{\sim}{X} - \underset{\sim}{X}(n)\right] \tag{4}$$

where A (n) is the n-state matrix equivalent of A (o) and $\underset{\sim}{X}$ (n) represents the n-state equilibrium configuration. The inverse transformation is

$$\underset{\sim}{X} = A^{+}(n)\,\underset{\sim}{q}(n) + \underset{\sim}{X}_{o}(n), \tag{5}$$

where

$$A(n)\,A^{+}(n) = II \tag{6}$$

In order to obtain a relationship between $\underset{\sim}{q}$ (o) and $\underset{\sim}{q}$ (n) we eliminate $\underset{\sim}{X}$ between Eqs. (2) and (5). The result is:

$$\underset{\sim}{q}(n) = B(n,o)\,\underset{\sim}{q}(o) - \Delta\underset{\sim}{Q}(n,o) \tag{7}$$

where

$$B(n,o) = A(n)\,A^{+}(o) \tag{8}$$

and

$$\Delta\underset{\sim}{Q}(n,o) = A(n)\left[\underset{\sim}{X}_{o}(n) - \underset{\sim}{X}_{o}(o)\right] \tag{9}$$

Since A (n) and A (o) are unitary, it follows from Eq. (8) that B (n,o) is unitary. From Eq. (7) we see that the excited state normal coordinates can be obtained from the ground state set by unitary transformations. And in this sense the ground state set acts as a basis. There is one other relationship required to complete the picture, namely that between two excited state normal coordinate vectors, say $\underset{\sim}{q}(n)$ and $\underset{\sim}{q}(k)$. The inverse of Eq. (7) is,

$$\underset{\sim}{q}\ (o) = B^{+}(k,o)\left[\underset{\sim}{q}(k) + \Delta\underset{\sim}{Q}(k,o)\right] \tag{10}$$

Substituting this relationship back into (8) yields

$$\underset{\sim}{q}(n) = B\ (n,k)\ \underset{\sim}{q}(k) - \Delta\underset{\sim}{Q}(n,k) \tag{11}$$

where

$$B\ (n,k) = B\ (n)\ B^{+}(k) \tag{12}$$

and

$$\Delta\underset{\sim}{Q}\ (n,k) = A\ (n)\left[\underset{\sim}{X}_{o}(n) - \underset{\sim}{X}_{o}(k)\right] \tag{13}$$

III. Trapping Energy

We assume that to each bound electron state, there corresponds a lattice equilibrium configuration. In accord with the "adiabatic-harmonic" approximation, we expand the electron eigenenergy to second order about the corresponding equilibrium configuration. Thus

$$E_n\ (\underset{\sim}{R}) = E_n\ (\underset{\sim}{R}_n) + 1/2\ \Sigma_j \omega_j^{\ 2}(n)\ q_j^{\ 2}(n), \tag{14}$$

where the equilibrium configuration is defined by

$$\left[\frac{\partial E_n}{\partial \underset{\sim}{R}}\ (\underset{\sim}{R})\right]_{\underset{\sim}{R}_n} = 0 \tag{15}$$

In these equations, $\underset{\sim}{R}$ represents the lattice configuration at any time, $\underset{\sim}{R}_n$ the equilibrium configuration, ω_j (n), the jth phonon eigenfrequency and q_j (n) the jth normal coordinate corresponding to the electron state n.

We define the trapping energy for a transition between state r and s as:

$$\Delta E_{r,s} = E_r (\underset{\sim}{R}) - E_s (\underset{\sim}{R}) \tag{16}$$

In terms of Eq. (14), this may be written as

$$\Delta E_{r,s} = E_r (\underset{\sim}{R}_r) - E_s (\underset{\sim}{R}_s) + 1/2\ \Sigma_j \omega_j^2(r)\ q_j^2(r) - 1/2\ \Sigma_j \omega_j^2(s)\ q_j^2(s) \tag{17}$$

This equation may be expressed entirely in terms of the s - state normal coordinates, q_j (s), by means of Eq. (11). The results is:

$$\Delta E_{r,s} = E_r (\underset{\sim}{R}_r) - E_s (\underset{\sim}{R}_s) + 1/2\Sigma_j \omega_j^2(r)\ \Delta Q_j^2(r,s) + 1/2\Sigma_{j,k,l}\ \omega_j^2(r) b_{jk}(r,s)$$

$$b_{jl}(r,s)\ q_k(s)\ q_\ell(s) - \Sigma_{j,k} \omega_j^2(r)\ b_{jk}(r,s) q_k(s)\ \Delta Q_j(r,s)$$

$$-1/2\Sigma_j\ \omega_j^2(s)\ q_j^2(s) \tag{18}$$

where $b_{jk}(r,s)$ represents the jkth element of the matrix B (r,s) defined by Eq. (12). If the transition proceeds vertically upward from the "s-state" equilibrium configuration $\underset{\sim}{q}(s) = \underset{\sim}{0}$, Eq. (18) reduces to:

$$\Delta E_{r,s}(\underset{\sim}{R}_s) = E_r(\underset{\sim}{R}_r) - E_s(\underset{\sim}{R}_s) + 1/2\Sigma\, \omega_j^2(r)\, \Delta Q_j^2(r,s) \tag{19}$$

This corresponds to <u>absorption</u> in which the amount of energy stored in the "r-state" lattice is:

$$1/2\Sigma_j \omega_j^2(r)\, \Delta Q_j^2(r,s) \tag{20}$$

It is also possible to express Eq. (17) in the terms of the "r-state" normal coordinates, $q_j(r)$, by means of Eq. (11). Following the same procedure as indicated above we find that if the transition proceeded vertically downward from the "r-state" equilibrium configuration, $\underset{\sim}{q}(r) = \underset{\sim}{0}$, then

$$\Delta E_{r,s}(\underset{\sim}{R}_r) = E_r(\underset{\sim}{R}_s) - E_s(\underset{\sim}{R}_s) - 1/2\Sigma_j \omega_j^2(s)\, \Delta Q_j^2(s,r) \tag{21}$$

This corresponds to emission in which the amount of energy stored in the "s-state" lattice is:

$$1/2\Sigma_j\ \omega_j^{\ 2}(s)\ \Delta Q_j^{\ 2}(s,r) \tag{22}$$

The Stokes Shift is simply the difference between Eqs. (19) and (20), namely

$$\Delta E = 1/2\Sigma_j\omega_j^{\ 2}(r)\ \Delta Q_j^{\ 2}(r,s) + 1/2\Sigma_j\ \omega_j^{\ 2}(s)\ \Delta Q_j^{\ 2}(s,r) \tag{23}$$

Figure 1. illustrates the above ideas in a one dimensional configuration coordinate diagram.

If we assume the existance of effective frequencies associated with these states[5,6], then Eq. (23) reduces to

$$\Delta E = \left[\omega^2(r) + \omega^2(s)\right] \Sigma_j\ \Delta X_{oj}^{\ 2}(r,s), \tag{24}$$

where

$$\Delta X_{oj}(r,s) = \left[X_o(r) - X_o(s)\right]_j \tag{25}$$

The Stokes Shift as described by Eq. (24) is of the correct order of magnitude for the F-center, in the alkali halides. Details of the calculation are discussed in Section V.

IV. Huang - Rhys Factors

In this section, we develop a rigorous formulation of the Huang-Rhys factors for the absorption and emission of light by deep electron traps. We shall concentrate on verticle transitions between two bound states s, and r. Once the general form has been constructed the special case of the F-band will be considered. Here the important states are "s-like" and "p-like". The guide lines for such a calculation have been laid out in a recent publication.[8] Accordingly we define the factors for absorption and emission as:

$$S_a = \Sigma_j \alpha_j N_j(r) \tag{26}$$

and

$$S_e = \Sigma_j \alpha^{-1} N_j(s) \tag{26a}$$

Here $N_j(s,r)$ and $N_j(r,s)$ represent the number of phonons stored in the jth lattice modes corresponding to the trapped electron states r, and s, respectively and α_j is a weighting factor defined as:

$$\alpha_j = \omega_j(r)/\omega_j(s) \tag{27}$$

From Eqs. (20) and (22)

$$N_j(r) = \omega_j(r)\ \Delta Q_j^2(r,s)/2\hbar \tag{28}$$

and

$$N_j(s) = \omega_j(s)\ \Delta\ Q_j^{\ 2}(s,r)/2\hbar \tag{29}$$

The general forms for the Huang-Rhys factors may now be expressed as:

$$S_a = \Sigma_{j,k,\ell}\ \alpha_j\ \omega_j(r)\ a\ (r)_{jk}\ a(r)_{j\ell}\ \Delta X_{ok}(r,s)\ \Delta X_{o\ell}(r,s)/2\hbar \tag{30}$$

and

$$S_e = \Sigma_{j,k,\ell}\ \alpha_j^{-1}\ \omega_j(s)\ a\ (s)_{jk}\ a(s)_{j\ell}\ \Delta X_{ok}(s,r)\ \Delta X_{o\ell}(s,r)/2\hbar \tag{31}$$

where we have used Eq.(13) in component form. Eqs. (30) and (31) are completely general expressions for the Huang-Rhys factors within the framework of the "adiabatic-harmonic" approximation.

In order to compare these results with those previously published, we introduce the following parameter:

$$e_k(s) = \left[\frac{\partial \Delta E_{r,s}}{\partial q_k(s)}\right]_{\underset{\sim}{R}_s}$$

From Eq. (18) and the companion equation expressed in terms of the coordinate $\underset{\sim}{q}_j(r)$, we have

$$e_k(s) = \Sigma_j \omega_j^2(r)\ b_{jk}(r,s)\ \Delta Q_j(r,s) \tag{33}$$

and

$$e_k(r) = \Sigma_j \omega_j^2(s)\ b_{jk}(s,r)\ \Delta Q_j(s,r) \tag{34}$$

From these equations and the unitary character of the b_{jk}'s, one can easily determine the inverse relationships for the ΔQ_j's. Substituting the ΔQ_j's as thus determined into Eqs. (30) and (31) yields the following results:

$$S_a = \Sigma_{j,k,k'} \left[\ \omega_j(s)\ \omega_j^2(r)\ \right]^{-1} b_{jk}(r,s)\ b_{jk'}(r,s)\ e_k(s)\ e_{k'}(s)/2\hbar \tag{35}$$

and

$$S_e = \Sigma_{j,k,k'} \left[\ \omega_j(r)\ \omega_j^2(s)\ \right]^{-1} b_{jk}(s,r)\ b_{jk'}(s,r)\ e_k(r)\ e_{k'}(r)/2\hbar$$

where the b_{jk}'s are assumed to be real. The reader will notice that if the existance of effective frequencies is assumed, then Eqs. (35) and (36) agree identically with the previous published results.[8]

The contrast between the two results may be further illustrated by considering the F-center in the alkali-halides. We assume a tight binding approximation,[9] and restrict our attention to the interaction between the F-center electron and its nearest neighbors. This seems to be a reasonable first approximation in light of Eqs. (30) and (31). Also we shall assume that the transitions take place between "s-like" and "p-like" states. On this basis it has been shown in reference (8) that:

$$e_k\,(s) = e_k\,(p) = 0, \tag{37}$$

for all values of $k \neq 1,3$. Using the results of the B-Matrix described in the Appendix, Eqs. (35) and (36) reduce to:

$$S_a = \Sigma_{j=1,3} \left[2\hbar\omega_j^{\,2}(p)\right]^{-1} e_j^{\,2}(s) + \Delta^2 Fa \tag{38}$$

and

$$S_e = \Sigma_{j=1,3} \left[2\hbar\omega_j(p)\omega_j^{\,2}(s)\right]^{-1} e_j^{\,2}(p) + \Delta^2 Fe \tag{39}$$

Here

$$F_a = \left[\left(\omega_3(s)\omega_3^{\,2}(p)\right)^{-1} e_1^{\,2}(s) + \left(\omega_1(s)\omega_1^{\,2}(p)\right)^{-1} e_3^{\,2}(s)\right]/6\hbar \tag{40}$$

and

$$F_e = \left[\left(\omega_3(p)\ \omega_3^{\,2}(s)\right)^{-1} e_1^{\,2}(p) + \left(\omega_1(p)\ \omega_1^{\,2}(s)\right)^{-1} e_3^{\,2}(p)\right]/6\hbar$$

and Δ is a lattice distortion parameter of order 4×10^{-2} angstroms.[10] A comparison of Eqs. (38), (39) and the forms used in reference (8) shows that they agree exactly if terms of order Δ^2 are ignored. Thus the present formulation includes the previous one as a special case. There is one other distinct advantage. The determination of the Huang-Rhys factors in the present formulation, involves essentially one piece of information, namely the lattice equilibrium configuration as a function of F-center electron state. Once this is known, then, in principle at least, the eigenfrequencies and the eigenvectors can be determined. With the eigenvectors one may then construct the A and B-matrices. But this solves the problem. In contrast, the previous formulation involved the determination of Feynman-Hellman integrals, in addition to the normal mode calculations indicated above.

V. Numerical Results

In this section, all calculations will be based on a tight binding approximation. We assume that the dominant electron-phonon interactions are localized in the vicinity of the trapped F-center electron. Therefore, we treat the center essentially as a molecule[8] possessing O_h symmetry in the electron ground state (s-like) and D_{4h} symmetry in the excited state (p-like). Figure 2. illustrates the model. This approximation is discussed in more detail in the Appendix.

The calculations to be considered are (a) the number of stored phonons, (b) the Huang-Rhys factors, and (c) the Stokes Shift for the F-center in various alkali halides. The experimental results of Gebhardt and Kuhnert[11] for the F-center absorption and emission half-widths and effective frequencies will be used. In addition use will be made of the theoretical results of Wood & Joy for the lattice distortion.

Stored Phonons

From Eqs. (28) and (29), the number of phonons stored in the jth mode of the lattice for the "p-like" electron state is:

$$N_j(p) = \omega_j(p)\ \Delta Q_j^{\,2}(p,s)/2\hbar \tag{42}$$

and for the "s-like" state is:

$$N_j(s) = \omega_j(s)\ \Delta Q_j^{\,2}(s,p)/2\hbar \tag{43}$$

The ΔQ_j's as defined by Eq. (13), are functions of the appropriate A-matrix and the equilibrium displacement coordinates. The matrices are shown in the appendix and the displacement coordinates are known from reference[10]. For all of the alkali halides considered, there are only two non-vanishing ΔQ_j's, namely ΔQ_1 and ΔQ_3. However, $\Delta Q_1/\Delta Q_3 \cong 50$. This indicates that an effective mode approximation is in order. This mode is the A_{1g} mode of the O_h group for the "s-like" state and the A_{1g} mode of the D_{4h} group for the "p-like" state.[8] As a result Eqs. (42) and (43) reduce to:

$$N(p) = M_+(p)\ \omega(p)\ \Sigma_k(\Delta X_k)^2/2\hbar \tag{44}$$

and

$$N(s) = M_+(s)\ \omega(s)\ \Sigma_k\ (\Delta X_k)^2/2\hbar \tag{45}$$

Here $M_+(p)$ and $M_+(s)$ represent the effective alkali ion mass and $\omega(p)$ and $\omega(s)$, the effective lattice frequency in the "p-like" and "s-like" state respectively. ΔX_k is simply the difference between the equilibrium positions of the kth ion as measured in the "p-like" and "s-like" state.

Effective Masses

In order to determine $M_+(p)$ and $M_+(s)$ we must consider the half widths of the F-bands. The absorption and emission half widths (extrapolated to 0^oK) as formulated by Klick[12] and Luty and Gebhardt[6] are:

$$H^2_{abs} = (8\ \ln\ 2)\left[\hbar^2\ \omega(s)\ \omega(p)\ N(a)\right](K_e/K_g) \tag{46a}$$

and

$$H^2_{em} = (8\ \ln\ 2)\left[\hbar^2\ \omega(s)\ \omega(p)\ N(e)\right](K_g/K_e \tag{46b}$$

where

$$N(a) = K_e X_o^{\ 2}/2\hbar\ \omega(p) \tag{47a}$$

and

$$N(e) = K_g X_o^{\ 2}/2\hbar\ \omega(s) \tag{47b}$$

Here K_e and K_g represent the effective excited and ground state spring constants and X_o, and effective lattice displacement. N (a) and N (e) are the number of phonons stored in the excited and ground state lattice. It should be noted that we are identifying the excited state with a "p-like" state, and the ground state with and "s-like" state.

From Eqs. (46) and (47) the following result is obtained

$$K_e/K_g = \left[\omega(p)\ H\bar{a}bs^2/\omega(s)\ H\bar{e}m^2\right]^{1/3} \tag{48}$$

By definition[5]

$$M_+(s) = K_g/\omega(p)^2 \tag{49a}$$

and

$$M_+(s) = K_g/\omega(s)^2 \tag{49b}$$

Therefore

$$M_+(p)/M_+(s) = \left[\omega(s)^5\ Habs^2/\ \omega(p)^5\ Hem^2\right]^{1/3} \tag{50}$$

Since the "s-like" F-center wave function is basically localized within the space defined by the six nearest neighbor ions[13], we assume with Luty that $M_+(s) \cong M_+$, the mass of the alkali ion.

Determination of $\Sigma_k(\Delta X_k)^2$

In the F-center ground state, the six nearest neighbor ions are radially displaced by an amount, δ, toward the center so that the symmetry remains as O_h. In the excited state the symmetry is D_{4h}. The two particles located on the C_4 axis, (particles 5 and 6 in Fig. 1(b), are displaced radially outward by δ_2' and the four remaining ions, by δ'_1. The δ's we use refer to actual displacements and are related to those used by Wood and Joy by the appropriate nearest neighbor distance. Using their results and those we have derived in the appendix yields the following expression:

$$\Sigma_k\ (\Delta X_k)^2 = 4\Delta_1{}^2 + 2\Delta_2{}^2, \tag{51}$$

where

$$\Delta_1 = \delta_1' - \delta \text{ and } \Delta_2 = \delta_2' - \delta \tag{52}$$

It should be noted that we are using the convention that outward displacements are positive. Thus δ is actually a negative number.

In order to compare our results with the recent experiments of Gebhardt and Kuhnert, we first consider their formulation of the half width equations, at 0^oK, namely

$$H^2_{abs} = (8\ \ell n\ 2)\ (\hbar\omega(p))^2 S_a' \tag{53}$$

and

$$\mathrm{Hem}^2 = (8\ \ln 2)\left(\hbar\omega(s)\right)^2 S_a'^{\,1} \tag{54}$$

Comparing these Eqs. with Eqs. (46), we find that

$$N_a = \left[\omega(p)\ \mathrm{Hem}/\omega(s)\ \mathrm{Habs}\right]^{2/3} S_a' \tag{55}$$

and

$$N_e = \left[\omega(s)\ \mathrm{Hab}/\omega(p)\ \mathrm{Hem}\right]^{2/3} S_e' \tag{56}$$

Since all of the terms on the right hand side of these equations are determined experimentally, N_a and N_e are specified experimentally. It is therefore, with Eqs. (55) and (56) that we compare our calculated results for the number of stored phonons.

A comparison between the Huang-Rhys factors as theoretically calculated and as determined experimentally by Gebhardt and Kuhnert is not possible. This is because of an inconsistent interpretation of these factors in their work. They identify the number of stored phonons with the Huang-Rhys factors. It has been pointed out in a recent publication[8] and it is evident from Eqs. (55) and (56) that this is not the case. This fact may account for the disparity between their results for the Huang-Rhys factors and other authors[6,14,15]. The Huang-Rhys factors for the alkali halides considered in Table 1 should be approximately 30±5 for absorption and the emission values are not expected to be significantly different[6,14-16].

To determine the Stokes Shift, we use Eq. (23) together with Eqs. (42) and (43). The result, in the effective mode approximation is,

$$\Delta E = \hbar\omega(p)\ N\ (p) + \hbar\omega(s)\ N\ (s) \tag{57}$$

In a configuration coordinate scheme, this is simply the difference in peak energies between the absorption and emission F-bands. The numerical results of our calculations are displayed in Table 1. From this table we see that the calculated results are in fair agreement with experiment. Or the bases of our "molecular" model and the accompanying simplifications this is the most that could be realistically expected. There are several features, however, which are worth noticing. First, the effective masses are functions of the F-center electron state. These masses are introduced in an attempt to account for differences in the trapped electron-phonon interactions. Since such interactions are clearly dependent on the electron state, this result is not surprising. Secondly, we see that the calculared values for the number of phonons stored in the excited state lattice, N(p). This is in agreement with the experimental results. Thirdly, the calculated values of the Huang-Rhys factors are of the correct order of magnitude. Finally, the calculated Stokes Shifts are consistantly low by roughly 30 to 40 per cent. We feel that this is a result of our single mode formulation. Recent results indicate that modes other than the simple breathing mode should be included in these F-center calculations[17,18]. This problem is discussed further in the next section.

Summary Discussion of Results

On the basis of an "adiabatic-harmonic" approximation it has been shown that the trapped electron eigenenergy for any state, n, may be represented in terms of a basis set of normal coordinates. The transformations relating different sets of normal coordinates have been developed. These transformations are unitary and depend on the local symmetry of the lattice surrounding the trap. Utilizing these transformations, we have derived general forms for the (a) the number of stored phonons, (b) the Stokes Shift, and (c) the Huang-Rhys factors.

Explicit calculations were then carried out for a tight binding model of the F-center in the alkali halides. With presently available data it was found that the major contribution to terms (a), (b) and (c) above, came from the A_{1g} modes of the O_h ("s-like" state) and the D_{4h} ("p-like" state) groups. These modes correspond to a pure breathing mode in the "s-like" state and to a perturbed breathing mode in the "p-like" state.

Although the numerical results of the calculation, shown in Table 1 indicate approximate agreement with experiment, the calculated Stokes' Shifts are consistantly low. Apparently, this is a manifestation of an inherent difficulty in the one-dimensional configuration coordinate scheme. On such a basis, there seems to be no consistent way of interpreting both absorption and emission phenomena. We feel that the discrepancy in the Stokes Shift arises primarily from a failure to take into account all of the important modes. A significant (20%) variation in the distortion parameters would most certainly bring in other significant model contributions. Very recent work by R. F. Wood indicates that such a variation may indeed exist.

The agreement between our calculations and the experimental results is rather surprising, especially in the case of emission. It should be recalled that we used the tight binding approximation of the F-center for both absorption and emission. While such an approximation of the F-center for both absorption and emission. While such an approximation may be valid for absorption, it is certainly questionable in the case of emission. This is because the relaxed "p-like" electronic charge distribution apparently spreads over several lattice constants[19]. Therefore one expects the localized electron-phonon interaction assumed in the tight binding approximation to break down. Of course it is still possible that the lattice distortion remains localized, in which case our formulation for the emission processes should be valid. This remains an open question.

In conclusion, there is no intrinsic reason to restrict the present formulation to deep electron traps such as the F-center. The F-center in KCl, NaCl, and KBr merely provided convenient systems on which to test our analysis. The equations developed should apply to any deep trap, hole or electron in which the primary processes are electronic. One problem in which we are presently interested is the determination of the entries listed in Table 1. for the system KCl:Tl Klick and co-workers have shown that the system cannot be interpreted on the basis of a simple one dimensional configuration coordinate diagram. Our formulation is in no way restricted to such a scheme. Furthermore, although the Tl^+ ion is large its charge distribution is apparently quite localized in both the ground and excited states. This means that the problem should even be amenable to out tight binding approximation.

APPENDIX I

The matrix, A(0), corresponding to an "s-like" ground state for the F-center has been determined[21]. In addition, a recent article[8] describes the technique for obtaining A(n), the matrix corresponding to a "p-like" excited state of the F-center. In this appendix we shall simply sketch the method and write down the results.

In the harmonic approximation, the potential functions for a system of interacting nuclei and electrons is:

$$V = 1/2\Sigma_{i,j} \left(\frac{\partial^2 V}{\partial X_i \partial X_j}\right)_{\underset{\sim}{R}_n} X_i X_j \tag{58A}$$

Here X_i represents the ith component of a 3N - dimensional, mass normalized, ion displacement vector[4] corresponding to the electron state n. $\underset{\sim}{R}_n$ represents the corresponding equilibrium configuration.

Equation (1) may be written in matrix form as

$$V = 1/2\, \underset{\sim}{\tilde{X}}\, V\, \underset{\sim}{X} \tag{59A}$$

where the meaning of the terms should be clear from a comparison with Eq. (1). We introduce a normal coordinate vector $\underset{\sim}{q}(n)$ corresponding to the state n as follows:

$$\underset{\sim}{q}(n) = A\,(n)\, \underset{\sim}{X} \tag{60A}$$

The inverse relationship is:

$$\underset{\sim}{X} = A^{+}(n)\, \underset{\sim}{q}\,(n) \tag{61A}$$

where $A^{+}(n)$ is the conjugate transpose of A, such that

$$A(n)\, A^{+}(n) = II \tag{62A}$$

Inserting this information back into (2) yields

$$V = 1/2\ \tilde{\underset{\sim}{q}}\ \lambda\ \underset{\sim}{q}, \text{ where} \tag{63A}$$

λ is the diagonal matrix determined by

$$AVA^{+} = \lambda \tag{64A}$$

In explicit form Eq. (6) becomes

$$V = 1/2\ \Sigma_j\ \omega_j^{\ 2}(n)\ q_j^{\ 2}(n) \tag{65A}$$

We now restrict our consideration to the tight binding approximation of the F-center[9]. The important interactions are assumed to take place within the cluster of particles surrounding the F-center electron. Figure 2 illustrates the model in both the ground and excited states. The significance of the core particle is discussed in reference[8]. The coupling constants between the ions is $K_{g,u}$, and that between the ions and the core particle is $K'_{g,u}$ depending on the electron state (ground, g; excited, u). The ground state normal modes for this model have been determined, and the corresponding excited state calculation has been outlined.[8]

In the present case we are interested only in the eigenvectors, which of course, determine the matrices A(0) and A(n)* - The calculation is simplified, although not essentially changed, by assuming that the K's vanich is both the ground and excited states. The resulting matrices are shown in Figs. 3 and 4 and the corresponding elements are given in Table 2 and 3. It should be noted that terms of order Δ^n, when n >1, have been neglected. The eigenfrequencies may be determined from Tables 1 and 2 of reference[8] by simply letting $K'=0$. The reader will note that

$$\lim_{\Delta \to 0} A(p) = A(s)$$

and

$$\lim_{\Delta \to 0} \omega_j(p) = \omega_j(s)$$

*The discreet eigenfrequency spectrum has been established for both the excited and ground state in reference[8].

which indicates that the results are at least consistent.

The matrix B, which is illustrated in Fig. 3 is determined by the relationship

$$B(p,s) = A(p)\ A^{+}(s) \tag{66A}$$

It can be seen from inspection that:

$$B = II + K \tag{67A}$$

where I is the identity matrix and K is an anti-symmetry matris of order Δ. Finally it is not difficult to see that

$$BB^{+} = I \tag{68A}$$

where terms of order Δ^2 are neglected - This is consistent without scheme of approximation.

REFERENCES

1. Markham, J. J., Rev. Mod. Phys. 31, 956 (1959)

2. Feynman, R. P., Phys. Rev. 56, 340 (1939)

3. Hellman, H., Einfuhrung in die Quanten Chemie, P. 285. Teuber, Leipzig (1937)

4. Born M. and Huang K., Dynamical Theory of Crystal Lattices, Chap. 4. Clarendon Press, Oxford (1954)

5. Klick, C. C., Phys. Rev. 85 154 (1952)

6. Luty, F. and Gebhardt, W., Z. Physik 169, 475 (1962)

7. Huang, K. and Rhys A., Proc. Roy. Soc. (Lond.) A204, 406 (1950)

8. Lemos, A. M. and Markham J. J. Phys. Chem. Solids 26, 1937 (1965)

9. Dexter D. L., Solid State Physics (eds. Seitz F. and Turnbull D.) Vol. 6 Academic Press, New York (1958).

10. Wood, R. F. and Joy H. W., Phys. Rev. 136, A451 (1964)

11. Gebhardt, W. and Kunhert H., Phys. Letters (Netherlands) 11, 15 (1964).

12. Klick C. C. and Schulman J. H., Solids State Physics (eds. Seitz F. and Turnbull D.) Vol. 5 Academic Press, New York (1957).

13. Gourary B. S. and Adrian F. J. Solid State Physics (eds. Seitz F. and Turnbull D.) Vol. 10 Academic Press, New York (1960)

14. Konitzer J. D. and Markham J. J., J. Chem. Phys. 32, 843 (1960)

15. Konitzer J. D. and Markham J. J., J. Chem. 34, 1936 (1961).

16. Gebhardt W. (unpublished)

17. Schnatterly S. E., International Symposium - Color Centers in the Alkali Halides (University of Illinois, 11-13, October, (1965) A164, 126

18. Lemos A. M. , Bul. Am. Phys. Soc. 10, 306 (1965)

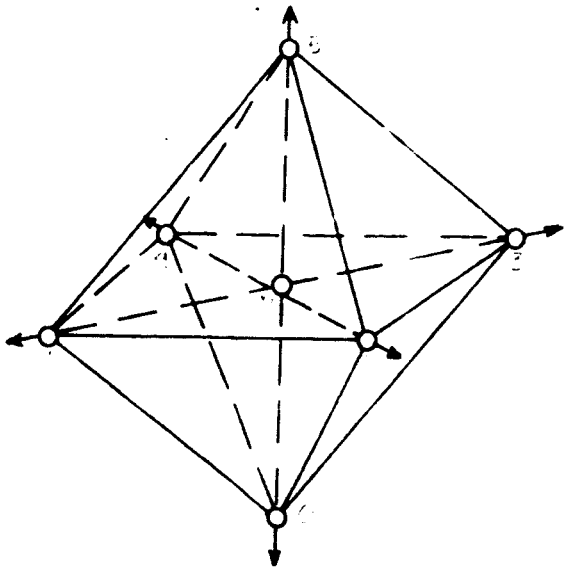
19. Fowler W. B., Phys. Rev. 135, A1725 (1964)

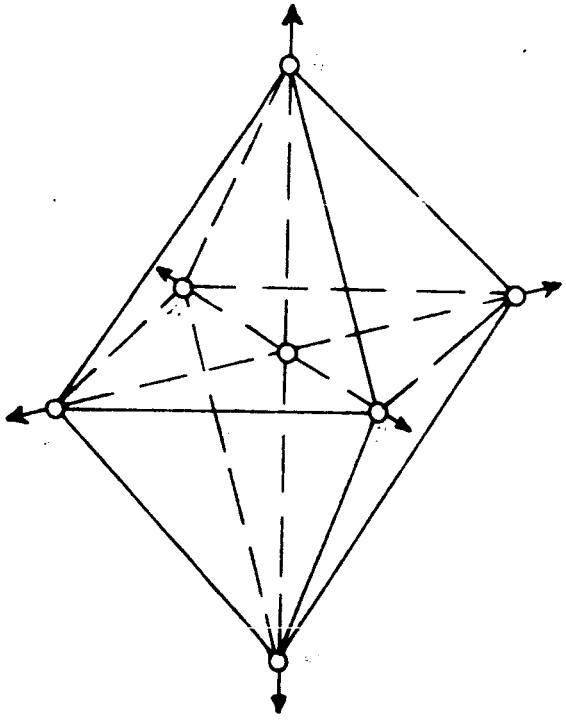
20. Williams, F. E., Phys. Rev. 82, 281 (1951)

21. Klick, C.C., Patterson D.A., Knox R. S, Phys. Rev. 133, A1717 (1964)

22. Lemos, A. M., Ph.D. Thesis, Illinois Institute of Technology (1964).

*Wood, R. F. - Private communication.





A A -A -A B -B

C -C -C C

D D -D -D -E E

F G F G -H -H

C -C C -C

G F G F -H -H

C C -C -C

I -I J -J

I -I J -J

-K L -K L M M

L -K L -K M M

N N N N -K -K

O O O O O O

O O O O O O

O O O O O O

C -C -C C

J -J -I I

J -J -I I

a		a		-a		-a		a		-a	
b		-b		-b		b					
c		c		-c		-c		-d		d	
	b				b		-b		-b		
	b		-b		b		-b				
		b				b		-b		-b	
	b	b			-b	-b					
	b				-b		b		-b		
			b				-b	b			-b
-d		c		-d		c		c		c	
	c		-d		c		-d		c		c
		c		c		c		c		-d	-d
a		a		a		a		a		a	
	a		a		a		a		a		a
		a		a		a		a		a	a
	b		-b		-b	b					
		b				-b		-b		b	
				b				-b	-b		b

Fig. 3A

	Reff.	$\Sigma(\Delta X_k)^2$ (Å)	$N_{cal}(p)$	$N_{exp}(p)$	$S_{cal}(a)$	$N_{cal}(s)$	$N_{exp}(s)$	$S_{cal}(e)$	ΔE_{cal} (e.v.)	ΔE_{exp} (p.v.)
NaCl	1.97	.659	20.7	28.8	27.8	30.6	42.5	25.4	1.085	1.695
KCl	2.81	.664	21.4	24.6	33.2	39.0	45.0	25.3	0.900	1.098
KBr	2.00	.710	25.3	28.0	34.2	37.8	41.6	28.2	0.846	1.148

TABLE 1