Lattice-Vibration Eigenvectors and Applications Thereof for NaCl and KCl†

S. S. JASWAL AND D. J. MONTGOMERY

Michigan State University, East Lansing, Michigan

(Received 3 April 1964)

Eigenvectors and eigenvalues for vibrations of the rocksalt lattice were computed in the harmonic approximation on the rigid-ion model and on a deformation-dipole model. The eigenvectors are useful in visualizing the actual motion of the ions in the normal modes, and thence for classifying the modes. The eigenvectors, furthermore, provide a basis for perturbation treatment. With them we have computed the frequencies of the local modes, and the corresponding amplitudes of impurity-atom vibrations, that result from point mass defects in NaCl and KCl.

INTRODUCTION

IN the harmonic approximation, the theory of lattice vibrations as set forth by Born and others[1] has been well worked out for some simple ionic crystals. Kellermann[2] used a rigid-ion model, and later workers[3] proposed more realistic models. Frequency calculations for perfect lattices on the basis of these later models satisfactorily describe the thermodynamic properties, and the dispersion curves from neutron scattering. Perturbation calculations, however, require knowledge of eigenvectors as well as eigenfrequencies. The New York University group, for example, has recently calculated the eigenvectors on the basis of the rigid-ion model for NaCl at room temperature,[4] and used them to determine the eigenfrequencies at low temperature[5] and the damping factor for infrared absorption.[6] In the present paper, we treat both NaCl and KCl on two models, the traditional rigid-ion (RI) model and the deformation-dipole (DD) model due to Hardy.[3] We give typical NaCl eigenvectors for the RI model, and show how the complete set of vectors serves for the classification of normal modes. On both RI and DD models we calculate the eigenfrequencies and the vibration amplitudes of the impurity atoms for the local modes due to point mass defects in the KCl and NaCl. The results are compared with theoretical calculations by others on different models, and with experimental findings for U centers.

THEORY

The equation of motion for small vibrations of particles in a periodic lattice may be written as

$$M_\kappa \ddot{u}_\alpha \binom{l}{\kappa} = \sum_{l'\kappa'\alpha'} \phi_{\alpha\alpha'} \binom{ll'}{\kappa\kappa'} u_{\alpha'} \binom{l'}{\kappa'}, \qquad (1)$$

where M_κ is the mass of the κth particle in the unit cell ($\kappa = 1, \cdots, s$, where s is the number of particles in the unit cell); $u_\alpha \binom{l}{\kappa}$ is the αth component of the displacement from equilibrium of the κth particle in the lth cell ($\alpha = 1, 2, 3; l = 1, \cdots, N$, where N is the total number of cells in the crystal); and where

$$\phi_{\alpha\alpha'} \binom{ll'}{\kappa\kappa'} \equiv [\partial^2\phi / \partial u_\alpha \binom{l}{\kappa} \partial u_{\alpha'} \binom{l'}{\kappa'}]_0,$$

with ϕ being the potential energy of the system.

With solutions of the form

$$u_\alpha \binom{l}{\kappa} = M_\kappa^{-1/2} u_\alpha(\kappa) \exp[-i\omega t + 2\pi i \mathbf{k} \cdot \mathbf{x} \binom{l}{\kappa}], \qquad (2)$$

we get

$$\omega^2 u_\alpha(\kappa) = \sum_{\kappa'\alpha'} D_{\alpha\alpha'} \binom{\mathbf{k}}{\kappa\kappa'} u_{\alpha'}(\kappa'), \qquad (3)$$

where the modified dynamical matrix $D_{\alpha\alpha'} \binom{\mathbf{k}}{\kappa\kappa'}$ is given by

$$D_{\alpha\alpha'} \binom{\mathbf{k}}{\kappa\kappa'} = -(M_\kappa M_{\kappa'})^{-1/2} \sum_{l'} \phi_{\alpha\alpha'} \binom{ll'}{\kappa\kappa'}$$

$$\times \exp[-2\pi i \mathbf{k} \cdot \{\mathbf{x} \binom{l}{\kappa} - \mathbf{x} \binom{l'}{\kappa'}\}]. \qquad (4)$$

In general, **D** is Hermitian, and by virtue of the geometric symmetry of the rock-salt structure it is real as well, and hence is symmetric.

For nontrivial solutions of Eq. (3) to exist, we must have

$$|\mathbf{D} - \omega^2 \mathbf{I}| = 0. \qquad (5)$$

For the rocksalt structure, this equation is of sixth degree in ω^2. Its roots give the eigenfrequencies of normal vibrational modes for a given wave vector $\mathbf{k}$.

† Supported by the U. S. Air Force Office of Scientific Research and the U. S. Atomic Energy Commission Division of Research.

[1] M. Born and T. von Karman, Physik Z. 13, 297 (1912); 14, 13 (1913); M. Born, *Dynamik der Kristallgitter* (B. G. Teubner, Leipzig, 1915); *Atomtheorie des festem Zustandes* (B. G. Teubner, Leipzig, 1923); Encyclopaedie der Mathematik 5, 527 (1926); M. Born and M. Goeppert-Mayer, *Handbuch der Physik*, edited by H. Geiger and Karl Scheel (Julius Springer, Berlin, 1933), Vol. 24, 2nd part; M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954).

[2] E. W. Kellermann, Phil. Trans. Roy. Soc. (London) 238, 513 (1940).

[3] K. B. Tolpygo, Zh. Eksperim. i Teor. Fiz. 20, 497 (1950); J. R. Hardy and A. M. Karo, Phil. Mag. 5, 859 (1960); J. R. Hardy, *ibid.* 7, 315 (1962); A. D. B. Woods, W. Cochran, and B. N. Brockhouse, Phys. Rev. 119, 980 (1960); A. D. B. Woods, B. N. Brockhouse, R. A. Cowley, and W. Cochran, *ibid.* 131, 1025 (1963); R. A. Cowley, W. Cochran, B. N. Brockhouse, and A. D. B. Woods, *ibid.* 131, 1030 (1963).

[4] J. Neuberger, Ph.D. thesis, Physics Department, New York University, 1958 (unpublished).

[5] E. M. Arase and R. D. Hatcher, J. Chem. Phys. 33, 1704 (1960).

[6] J. Neuberger and R. D. Hatcher, J. Chem. Phys. 34, 1733 (1961).

These modes correspond to six branches of dispersion curves, which are labeled by $j = 1, \cdots, 6$.

With **D** evaluated under the assumption of the rigid-ion model, and nearest-neighbor short-range interactions, Kellermann[2] solved Eq. (5) for NaCl. Other authors[7] applied the same method to some other ionic crystals having the NaCl structure. Later workers[3] made similar calculations with models more realistic than the rigid-ion one.

For a given wave vector, corresponding to each branch we can find a vector **w** whose components satisfy the equation

$$\omega_j{}^2(\mathbf{k})w_\alpha(\kappa\mid {}^{\mathbf{k}}_j) = \sum_{\kappa'\alpha'} D_{\alpha\alpha'}({}^{\mathbf{k}}_{\kappa\kappa'})w_{\alpha'}(\kappa'\mid{}^{\mathbf{k}}_j). \qquad (6)$$

These equations determine **w** within a constant factor. The arbitrariness in **w** can be removed by orthonormality conditions:

$$\sum_{\kappa\alpha} w_\alpha(\kappa\mid{}^{\mathbf{k}}_j)w_\alpha{}^*(\kappa\mid{}^{\mathbf{k}}_{j'}) = \delta_{jj'},$$

$$\sum_{j} w_\alpha(\kappa\mid{}^{\mathbf{k}}_j)w_{\alpha'}{}^*(\kappa'\mid{}^{\mathbf{k}}_j) = \delta_{\alpha\alpha'}\delta_{\kappa\kappa'}. \qquad (7)$$

This orthonormal set of **w**'s is the set of eigenvectors with which we are concerned here.

In matrix form, Eq. (6) can be written as

$$\mathbf{DS} = \mathbf{S}\omega^2$$

or

$$\mathbf{S}^{\mathrm{T}}\mathbf{DS} = \omega^2,$$

where the columns of **S** are the eigenvectors, and ω^2 is a diagonal matrix with the eigenvalues as the diagonal elements. Since **D** is real and symmetric, it can be diagonalized by an orthogonal matrix **S**.

The general motion of the lattice is given by a superposition of the elementary solutions (2):

$$u_\alpha({}^l_\kappa) = N^{-1/2}\sum_{\mathbf{k}j} M_\kappa{}^{-1/2}w_\alpha(\kappa\mid{}^{\mathbf{k}}_j)Q({}^{\mathbf{k}}_j)$$

$$\times \exp[-i\omega_j(\mathbf{k})t + 2\pi i \mathbf{k}\cdot\mathbf{x}({}^l_\kappa)]. \qquad (8)$$

RESULTS: PERFECT LATTICE

A modified Jacobi method was used to diagonalize **D** and thereby to obtain both the diagonalizing matrix **S** and the eigenvalues ω^2. The computations were made on the CDC-3600 computer at Michigan State University, with an adaptation of 704–709 FORTRAN program No. 664, CO–OP ID: F4 UCSD 1 EIGEN. The Coulomb terms in the modified dynamical matrix were taken from Kellermann for his division of **k** space ($k_x = p_x/10$, etc.).

In this treatment, calculations are made for 48 points in the first Brillouin zone, from which 1000 points are generated by symmetry operations. To see the effect of finer subdivision of **k** space on local-mode results, which are to be considered in the next section, we have carried out calculations also for $k_x = p_x/20$, etc., after summing Kellermann's series for the Coulomb terms. This subdivision gives 262 wave vectors, which generate 8000 points in the first zone by symmetry operations. The results in the present section, however, are based on Kellermann's subdivision, with the aim of facilitating comparison with his work.

To see what typical eigenvectors look like, we have chosen two wave vectors for NaCl, one in a direction of symmetry and the other in a general direction, and have presented the corresponding eigenvectors in Table I and Table II, respectively. These eigenvectors, when normalized through division by $(NM_\kappa)^{1/2}$, give the amplitudes of vibration for the two kinds of ions in a given mode. Each column gives the eigenvectors for a given mode (whose frequency is indicated at the top), the first three elements corresponding to the Cartesian components of displacement of one kind of ion, and the last three to those of the other.

For all the NaCl eigenvectors we have computed the ratio of the amplitudes of vibration for the two kinds of ions. We have calculated also the angle (Na,Cl) between the directions of motion for the two kinds of ions, and the angles (Na,**k**) and (Cl,**k**) between the directions of motion for each kind of ion and the direction of propagation of the wave.[8]

For **k** = 0, the ratio of the amplitudes of lighter to heavier atom is inversely proportional to their masses, in the optical branch; in general it increases with increasing **k**. The corresponding ratio in the acoustical branch is equal to unity; it decreases with increasing **k**. Then, by continuity, we can classify the normal modes into various branches, and state their character as to longitudinality, transversality, or neither. For **k** along [100], [110], and [111], the waves are purely transverse or longitudinal, and the direction of vibration of both kinds of ions is the same, as is apparent from the symmetry of the crystal structure. Also, in certain directions of somewhat lower symmetry, viz., either when one of the components of wave vector is zero, or when two components are equal, there exists a pair of transverse waves, one optical and one acoustic. In all other cases, the waves are neither transverse nor longitudinal, and the directions of vibrations of two ions are different.

[7] E. V. Sayre and J. J. Beaver, J. Chem. Phys. **18**, 584 (1950); A. M. Karo, *ibid*. **31**, 1489 (1959); **33**, 7 (1960).

TABLE I. NaCl lattice-vibration eigenvectors for wave propagation along the symmetry direction [10,0,0]/10.

j		1	2	3	4	5	6
$\omega_j(10^{13}/\text{sec})$		4.198	3.099	3.093	3.093	1.776	1.776
Na$^+$	w_x	-0.9284	-0.3716	0	0	0	0
	w_y	0	0	-0.8435	0	0	-0.5372
	w_z	0	0	0	-0.8435	-0.5372	0
Cl$^-$	w_x	0.3716	-0.9284	0	0	0	0
	w_y	0	0	0.5372	0	0	-0.8435
	w_z	0	0	0	0.5372	-0.8435	0

TABLE II. NaCl lattice-vibration eigenvectors for wave propagation along the nonsymmetry direction [9,5,1]/10.

j		1	2	3	4	5	6
$\omega_j(10^{13}/\text{sec})$		3.596	3.356	2.896	2.882	2.596	2.229
Na$^+$	w_x	-0.6435	-0.7022	-0.0052	-0.2421	-0.1651	-0.0830
	w_y	-0.4145	0	0	0.7465	0.5206	0
	w_z	-0.6435	-0.7022	0.0052	-0.2421	-0.1652	-0.0830
Cl$^-$	w_x	-0.0024	-0.0291	-0.6641	-0.4035	0.5807	0.2902
	w_y	0	0.1101	-0.4125	0	0	-0.9044
	w_z	-0.0032	-0.0291	-0.6441	0.4034	-0.5807	0.2902

RESULTS: IMPURITY MODES

In diatomic cubic crystals the eigenfrequencies $\omega^2(f)$ for the modes due to a single mass defect[9] are given by

$$1 = \frac{\epsilon_\kappa \omega^2(f)}{3N} \sum_{kj} \frac{|\mathbf{w}(\kappa|^{k}_{j})|^2}{\omega^2(f) - \omega_j^2(\mathbf{k})}, \tag{9}$$

where $\epsilon_\kappa \equiv (M_\kappa - M_\kappa')/M_\kappa$, with M_κ' as the mass of the isotopic impurity. The $\omega_j^2(\mathbf{k})$ refer to the modes of the unperturbed lattice, and the $\mathbf{w}$'s are the corresponding eigenvectors of the ion that has been replaced by the impurity. The corresponding amplitudes of vibration for the impurity atom $|\chi(f,0)|^2$ are given by

$$1/M_\kappa|\chi(f,0)|^2 = \frac{\epsilon_\kappa^2 \omega^4(f)}{3N} \sum_{kj} \frac{|\mathbf{w}(\kappa|^{k}_{j})|^2}{(\omega^2(f) - \omega_j^2(\mathbf{k}))^2} - \epsilon_\kappa. \tag{10}$$

We have used Eqs. (9) and (10), respectively, to compute the frequencies of infrared-active local modes lying above the optical branches, and the corresponding amplitudes of vibrations of impurity atom, as function of ϵ_{Cl} for both KCl and NaCl. We have made calculations with both Kellermann's subdivision of $\mathbf{k}$ space ($k_x = p_x/10$, etc.) and our finer subdivision ($k_x = p_x/20$, etc.). The two treatments give the same results, which are shown in Figs. 1–4. On the graphs are also shown the experimental findings for U centers,[10] and results of

theoretical calculations by others[11] treating U centers as isotopic impurities. Rosenstock treated KCl as a linear monatomic chain, with nearest-neighbor short-range interactions only. Wallis and Maradudin chose a three-dimensional monatomic model for KCl and a diatomic
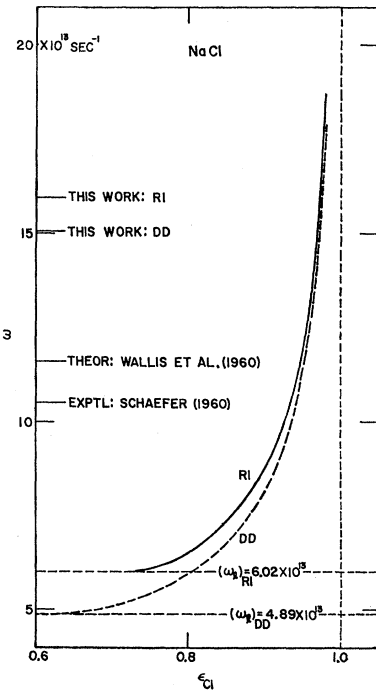

FIG. 1. Frequency of local modes in NaCl as a function of ϵ_{Cl}, on the basis of RI and DD models.

[9] A. A. Maradudin, 1962 Brandeis University Summer Institute Lectures in Theoretical Physics (W. A. Benjamin, Inc., New York, 1962), Vol. II; P. G. Dawber and R. J. Elliott, Proc. Roy. Soc. (London) A273, 222 (1963).
[10] G. Schaefer, Phys. Chem. Solids 12, 233 (1960); A. Mitsuishi and H. Yoshinaga, Progr. Theoret. Phys. (Kyoto) Suppl. No. 23 241 (1962).

[11] H. B. Rosenstock, Phys. Rev. 119, 1198 (1960); R. F. Wallis and A. A. Maradudin, Progr. Theoret. Phys. (Kyoto) 24, 1055 (1960).

TABLE III. Angular frequencies (in 10^{13} rad/sec) for impurity vibrations in NaCl and KCl.

Impurity mass	ϵ_{Cl}	Calculated eigenfrequencies				U center absorption		
		NaCl		KCl			NaCl	KCl
		RI $\omega(f)$	DD $\omega(f)$	RI $\omega(f)$	DD $\omega(f)$	Impurity ion	ω_0	ω_0
1.009	0.972	15.9	15.1	14.2	13.5	H$^-$	10.52	9.36
2.015	0.943	11.2	10.6	10.1	9.4	D$^-$	$\cdots$	6.73
Ratio		1.42	1.42	1.41	1.43			1.39

model for NaCl, with nearest-neighbor short-range interactions in each case.

With respect to our own results, we note first from Figs. 1 and 2 that the RI model gives somewhat higher frequencies for the local modes than the DD model, as would be expected. Next we see that there are critical values of ϵ_{Cl} for local modes to occur above the optical branches in both crystals. Table III gives the results from our calculations for the frequencies of local modes, and their ratio, corresponding to ϵ_{Cl} equal to 0.972 and 0.943, the values for H$^-$ and D$^-$, respectively. It contains as well the experimental results for the absorption frequencies observed for H$^-$ and D$^-$ in NaCl and KCl. The ratio given by our calculations is about the same as that of Wallis and Maradudin,[11] i.e., $\sim\sqrt{2}$. It is seen that experimental values are far lower than the calculated values on both models and for both crystals. On the other hand, the experimental ratio, available only for KCl, does agree quite well with the theory.

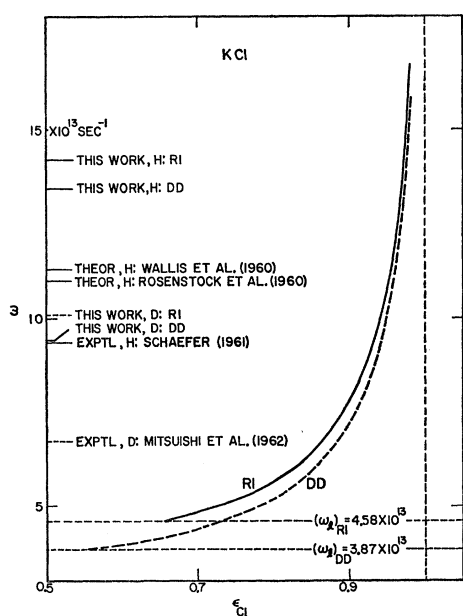Amplitude of vibration of impurity atom, given by

Figs. 3 and 4, increases with the decrease of mass of the impurity as expected.

Since the DD model gives good results for the perfect lattice, the poor agreement between our results and the experimental findings for U centers indicates that the U center cannot be treated as a simple isotopic impurity.
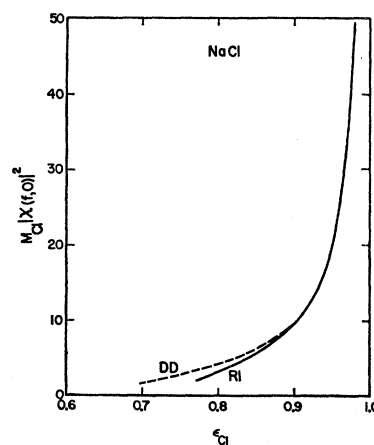

FIG. 3. Amplitude of vibration of impurity atom in NaCl, in terms of $M_{Cl}|x(f,0)|^2$, as a function of ϵ_{Cl}, on the basis of RI and DD models.
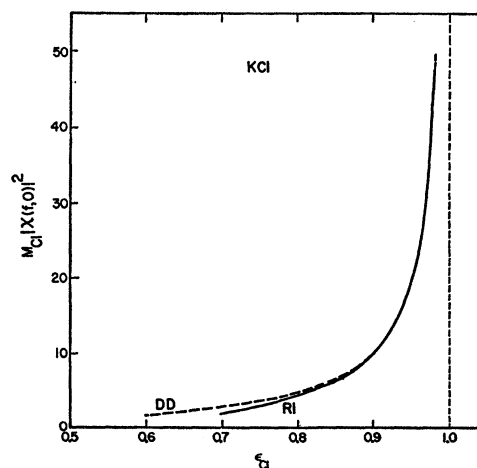

FIG. 4. Amplitude of vibration of impurity atom in KCl, in terms of $M_{Cl}|x(f,0)|^2$, as a function of ϵ_{Cl}, on the basis of RI and DD models.

FIG. 2. Frequencies of local modes in KCl as a function of ϵ_{Cl}, on the basis of RI and DD models.

The changes in force constants, polarization, and effective charge are large enough to have significant effect on the frequencies of defect modes. Unfortunately it would be extremely complicated to take these changes into account.

CONCLUSIONS

For wave vectors directed along axes of symmetry in the perfect rock-salt structure, the lattice-vibration waves are either purely transverse or purely longitudinal. For directions of somewhat lower symmetry, viz., when either one component of the wavevector is zero or two of them are equal, there is a pair of transverse waves. But for all other wave vectors, the waves are neither transverse nor longitudinal.

When isotopic impurities are introduced in the rock-salt lattice, local modes will appear above the optical branches for mass difference beyond a certain critical value.

Evidently it is inadequate to treat U centers in KCl and NaCl as simple isotopic impurities harmonically coupled to the lattice, without considering changes in force constants, polarization, and effective charge.

Pressure Dependence of the Electric Field Gradient in Metallic Indium*

W. J. O'SULLIVAN AND J. E. SCHIRBER

Sandia Laboratory, Albuquerque, New Mexico

(Received 6 April 1964)

The shift of the $^{115}\text{In}_{|7/2|\leftrightarrow|9/2|}$ nuclear quadrupole resonance (NQR) in indium metal has been measured at 25.5°C as a function of hydrostatic pressure to 8 kbar. In addition, the linear compressibilities at 25.5°C and the linear thermal-expansion coefficients and resonance-frequency temperature dependence in the room-temperature region were measured. Since the electric field gradient is a function of three variables, these measurements are insufficient to separate the explicit dependences. The obvious third experiment, the effect of uniaxial stress on the NQR, is not feasible, as it would require detection of the broad NQR of indium in the skin depth of a single crystal. We can therefore only infer that the major contribution to the change in field gradient is due to the change in distortion parameter $(c/a)-1$. A possible solution to this problem at one temperature is discussed.

I. INTRODUCTION

THE conduction-band contribution should be the major source of the nuclear-site electric field gradient (EFG) in metals which have noncubic structures and whose conduction bands evidence an appreciable degree of p-electron character. To date, nuclear quadrupole resonance NQR techniques have been applied to gallium[1,2] and indium [3-6] (two s- and one p-valence electron/atom) and antimony[7,8] ($5s^2\,5p^3$)

in an effort to assess the importance of the conduction electrons as a source of the EFG in metals.

In principle, information relating to the conduction-electron distribution could be extracted from a model which satisfactorily represents the EFG at the nuclear site in a metal. However, it is necessary that the criteria used to assess the merit of a model be detailed enough to be significant. A comparison between a theoretical value for the EFG and the experimental value at a single temperature and pressure is insufficient. We have therefore measured the effect of pressure on the NQR, the linear compressibilities, and the linear thermal expansivities in metallic indium, in order to enlarge the set of available criteria which may be used to check theoretical models of the electron-charge distribution in indium. Indium was chosen for this investigation because of its relatively simple structure and because there has been considerable interest in the fact that its quadrupole coupling parameter is extremely sensitive to temperature change.[9]

The indium lattice is most simply viewed as a fcc

[1] W. D. Knight, R. R. Hewitt, and M. Pomerantz, Phys. Rev. 104, 271 (1956).
[2] T. Kushida and G. Benedek, Bull. Am. Phys. Soc. 3, 167 (1958).
[3] R. R. Hewitt and W. D. Knight, Phys. Rev. Letters 3, 18 (1959).
[4] W. W. Simmons and C. P. Slichter, Phys. Rev. 121, 1580 (1961).
[5] W. J. O'Sullivan, W. A. Robinson, and W. W. Simmons, Bull. Am. Phys. Soc. 5, 413 (1960).
[6] R. R. Hewitt and T. T. Taylor, Phys. Rev. 125, 524 (1962).
[7] R. R. Hewitt and B. F. Williams, Phys. Rev. 129, 1180 (1963).
[8] T. T. Taylor and E. H. Hygh, Phys. Rev. 129, 1193 (1963).
[9] W. J. O'Sullivan and J. E. Schirber, Bull. Am. Phys. Soc. 9, 25 (1964).