G. R. Crane, J. Acoust. Soc. Am. 47, 791 (1970).

[6] W. Otaguro, C. A. Arguello, and S. P. S. Porto, Phys. Rev. B 1, 2818 (1970).

[7] W. S. Otaguro, E. Wiener-Avnear, and S. P. S. Porto, Appl. Phys. Letters (to be published).

[8] C. M. Hartwig, E. Wiener-Avnear, J. Smit, and S. P. S. Porto, Phys. Rev. B 3, 2078 (1971).

[9] J. Jerphagnon, Appl. Phys. Letters 16, 298 (1970).

[10] G. Nath, H. Mehmanesch, and M. Gsänger, Appl. Phys. Letters 17, 286 (1970) (previous report with a higher value for the SHG, Ref. 2).

[11] A. J. Campillo and C. L. Tang, Appl. Phys. Letters 16, 242 (1970); 16, 537(E) (1970).

[12] W. E. Dasent and T. C. Waddington, J. Chem. Soc. XX, 2429 (1960).

[13] C. Haas and D. F. Hornig, J. Chem. Phys. 26, 707 (1957); E. Burstein, in *Dynamical Processes in Solid State Optics*, edited by R. Kubo and H. Kamimura (Benjamin, New York, 1967), pp. 1–33.

[14] W. Cochran, Advan. Phys. 9, 387 (1960).

[15] M. Di Domenico, Jr., S. H. Wemple, and S. P. S. Porto, Phys. Rev. 174, 522 (1968).

[16] C. H. Henry and J. J. Hopfield, Phys. Rev. Letters 15, 964 (1965).

[17] S. P. S. Porto, B. Tell, and T. C. Damen, Phys. Rev. Letters 16, 450 (1966).

[18] E. Burstein, S. Ushioda, A. Pinczuk, and J. Scott, in *Proceedings of the International Conference on Light Scattering Spectra in Solids, New York University*, 1968, edited by G. B. Wright (Springer-Verlag, New York, 1969).

[19] C. A. Arguello, D. L. Rousseau, and S. P. S. Porto, Phys. Rev. 181, 1351 (1969).

[20] I. P. Kaminow, in *Ferroelectricity: Proceedings of the Symposium on Ferroelectricity, General Motors Research Laboratories, Warren, Mich.*, 1966 (Elsevier, Houston, Tex., 1966).

[21] I. P. Kaminow and W. D. Johnston, Jr., Phys. Rev. 160, 519 (1967); 178, 1528(E) (1969); W. D. Johnston Jr. and I. P. Kaminow, *ibid.* 188, 1209 (1969).

[22] Crystals were kindly sent to us by G. Nath, Physik-Department der Technischen Hochschule, München, München, Germany, and J. G. Bergman, Bell Telephone Laboratories, Murray Hill, N. J.

[23] E. Wiener-Avnear and S. P. S. Porto (unpublished).

[24] Lewis Fraas, thesis (University of Southern California, 1971) (unpublished).

[25] R. Claus, H. W. Schrotter, H. H. Hacher, and S. Haussuhl, Z. Naturforsch. 24a, 1733 (1969); R. Claus, *ibid.* 25a, 306 (1970).

[26] C. K. Asawa and M. K. Barnoski, Phys. Rev. B 3, 2682 (1971).

[27] J. G. Skinner and W. G. Nilsen, J. Opt. Soc. Am. 58, 113 (1968); P. E. Schoen, H. Z. Cummins, and R. L. Reese, Bull. Am. Phys. Soc. 16, 29 (1971).

[28] F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, New York, 1962).

[29] R. Loudon, Advan. Phys. 13, 423 (1966).

[30] C. K. Asawa, Phys. Rev. B 2, 2068 (1970).

[31] J. E. Bjorkholm, J. Quantum Electron. QE4, 970 (1968).

[32] S. E. Harris, Chromatix Tech. Letters 1, 1 (1969).

PHYSICAL REVIEW B VOLUME 4, NUMBER 12 15 DECEMBER 1971

Lattice Dynamics of KN$_3$

K. R. Rao,* S. F. Trevino,† and H. Prask†
Explosives Laboratory, Feltman Research Laboratory, Picatinny Arsenal, Dover, New Jersey 07801

and

R. D. Mical‡
Boston College, Chestnut Hill, Massachusetts 02167

(Received 21 June 1971)

In this paper we report the measurement of several acoustic-phonon modes in KN$_3$. Results for the longitudinal and doubly degenerate transverse modes along the $[00\mu]$ directions and the longitudinal and one transverse mode (polarized along the c axis) propogating along the $[\mu\mu0]$ direction are presented. The measurements are compared with a calculation based on a rigid-ion model. The model includes point charges at the position of the cation and at the center of the anion. The short-range repulsive interaction is a modified Huggins-Mayer potential with the cation treated as spherical and the anion as an ellipsoid of revolution. Adequate agreement is obtained with the present neutron-scattering measurement and with recent infrared and Raman results.

I. INTRODUCTION

Metal azide salts form an interesting family of materials which exhibit a broad range of crystal stabilities. The structure of most of the light-metal azides and several of the heavy-metal azides is known. In the light-metal azides, the azide ion is linear and symmetric, whereas in the heavy-metal salts, which are considerably less stable, there exist asymmetric and nonlinear azide ions. This has lead to the speculation that the interactions of the metal and azide ions change qualitatively between the light- and heavy-metal compounds. This difference in the type of bonding could be significant in explaining the markedly different stabilities. An investigation of the lattice dynamics of these crystals would seem a fruitful study for the purpose of testing these ideas.

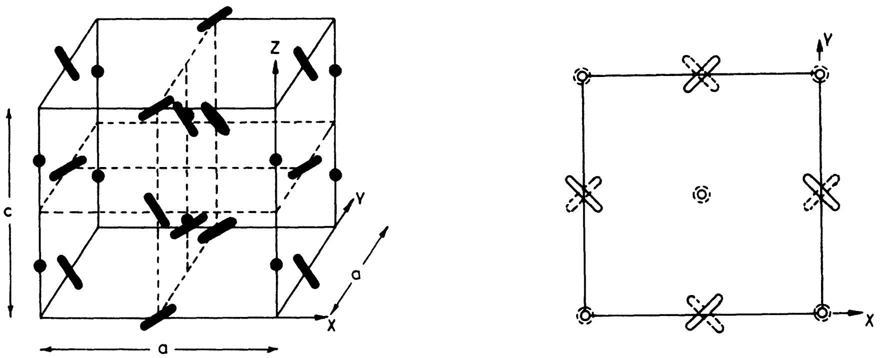

FIG. 1. Structure of KN_3. The circles and rodlike bodies are the potassium and azide ions, respectively.

We have chosen potassium azide (KN_3) for the initial study because of its relatively simple crystal structure and because single crystals could be grown from a water solution. KN_3 crystallizes in a body-centered tetragonal structure, with space group D_{4h}^{18}, containing two chemical units in the primitive cell (Fig. 1).[1] Most of the infrared and Raman studies have been directed to understand the internal vibrations of the azide ions. The side bands which accompany these fundamentals have been interpreted as being due to combinations with the optical lattice modes. An assignment has been made by Bryant[2] from this type of data and a lattice-dynamics calculation[3] has been made for $\vec{q}=0$ to match this assignment. More recently, Raman studies have been made by Iqbal[4] and Hathaway and Temple[5] in which the active lattice modes have been directly observed. Mitra[6] has measured the infrared reflectivity of single crystals of KN_3 and has identified the transverse and longitudinal modes. The results of these last two investigations are summarized in Table I. Several of Bryant's original assignments have been revised.

A group-theoretical analysis of the lattice dynamics of KN_3 has been published[7] and is used in the present work to aid in the identification of normal modes and in the model calculations.

In the present work, we present the measurement of the acoustic modes which propagate along the $[00\mu]$ or Λ and $[\mu\mu 0]$ or Σ directions. A model has been constructed which is used to calculate the dispersion curves along these two directions. The model introduces the Coulomb contribution due to the charge on the ions by the method employed by Kellerman.[8] The short-range repulsive potential is a modified Huggins-Mayer potential.[9] There are essentially two parameters, the charge and the repulsive strength, which are varied to reproduce the neutron data. Satisfactory agreement is attained with the present neutron data as well as with the infrared and Raman optical modes.

II. MODEL

The majority of models used in the calculation of the lattice dynamics of crystalline solids invoke the harmonic approximation. This consists of expanding the potential energy about the equilibrium positions of the particles and neglecting terms higher than quadratic. The details involved and limitations present have been thoroughly discussed in several texts and articles.[10] Dolling[11] has recently suggested using a coordinate system in which the center-of-mass translations and rigid-body rotation of molecular groups are used explicitly in the expansion of the potential. This technique is well suited to the description of the dynamics of molecular groups in which the internal vibrations of the molecule are of energies which are large with respect to the external vibrations, so that little coupling between the two would be expected to exist. The azide molecule adequately fullfills this criterion, so that in the present calculation this additional simplification is used.

The "force constants" which enter into the equations of motion have the form

$$\phi_{\alpha\beta}(\vec{l}, kk') = \frac{\partial^2 \phi[\vec{X}(\vec{l}, k)]}{\partial U_\alpha(\vec{0}, k)\, \partial U_\beta(\vec{l}, k)} , \qquad (1)$$

where $\phi[\vec{X}(\vec{l}, k)]$ is the potential energy which is a function of the instantaneous atomic position $\vec{X}(\vec{l}, k)$ of the kth particle in the $\vec{l}$th unit cell. $U_\alpha(\vec{0}, k)$ is the αth component of the displacement of the kth particle in the cell located at the origin and $U_\beta(\vec{l}, k')$ is the βth component of the displace-

TABLE I. Comparison of the $\vec{q}=0$ observed and calculated phonons.

Mode	Obs.[a,b]	Calc.[a]
LO (A_{2u})	150	166
TO (A_{2u})	130	108
LO $(E_u)_1$	196	189
TO $(E_u)_1$	162	145
LO $(E_u)_2$	150	147
TO $(E_u)_2$	130	130
T (E_g)	102[c]	108

[a] All frequencies in cm^{-1}. [c] From Refs. 4 and 5.
[b] From Ref. 6.

ment of the k'th particle in cell $\vec{l}$. α and β can be either Cartesian displacements of the center of mass of the molecules or can correspond to rotations about the Cartesian axes. The equations of motion are then written as functions of the force constants and the masses and moments of intertia of the various molecules. Instead of treating these force constants as adjustable parameters, we have derived them from explicit forms for the potential which includes a Coulomb interaction and a short-range repulsive potential of the Huggins-Mayer type.

Because of the preliminary nature of the experimental results a fairly drastic simplifying assumption was employed in the calculation. This consisted of neglecting any rotation-translation coupling. This assumption considerably simplified the construction of the dynamical problem. We are aware that the inclusion of rotation-translation coupling can alter the dispersion curves of low-frequency modes, as has been found by Schnepp and Ron[12] for the case of $\alpha - N_2$.

A. Coulomb Interaction

The effect of the ionic character of the crystal has been introduced by placing a positive point charge Ze at the position of each potassium and a negative point charge $-Ze$ at the center of the azide ion. The calculation of the force constants (1) due to these charges can then be accomplished by the method first employed by Kellerman[8] for NaCl. This technique consists of replacing a slowly converging sum over atomic position in the direct lattice by two rapidly converging series, one over the direct lattice and one over the reciprocal lattice. The calculation is quite straightforward and details can be found in Kellerman's original article, the text by Born and Huang, [10] and an article by Roy and Venkataraman. [13]

B. Repulsive Potential

Gray and Waddington[9] have used a modified Huggins-Mayer potential to calculate the lattice energies of various metal azide salts. We use this same type of potential in this calculation because it introduces a minimum of adjustable parameters and accounts for the finite size of the azide ion. The Huggins-Mayer potential has the form

$$V(\vec{r}_{kk'}) = bc\, e^{\vec{R}_k + \vec{R}_{k'} - \vec{r}_{kk'}/\rho} , \qquad (2)$$

where $\vec{R}_k$ and $\vec{R}_{k'}$ are the ionic radii, $\vec{r}_{kk'}$ is the separation of the centers of particles k and k', and ρ is an effective-range parameter. The factor c suggested by Pauling[14] accounts for the net charge and outer electronic configuration of the two ions. The values of 0.75, 1.0, and 1.25 have been suggested for this parameter, corresponding to k and k' being two negative ions, two ions of opposite charge, and two positive ions, respectively. We have used $\rho = 0.34$ Å as a fixed value from data on the alkali halides. The interaction strength b thus remains as the only adjustable parameter. The ionic radius of potassium is taken as 1.33 Å, the Goldschmidt radius. The azide ion is assumed to be an ellipsoid of revolution with major and minor axes of 4.04 and 2.8 Å. In the case of the $N_3^- - K^+$ interaction, the "radius" of the N_3^- ion is taken as 1.56 Å, which corresponds to the distance from the center of the ion to the surface of the ellipsoid along the line joining the centers of the N_3^- and K^+ ions. The calculation of the "force constants" using this potential has been performed for interactions between the first eight potassium-azides, the first 14 potassium-potassium, and the first 14 azide-azide neighbors.

The resulting model contains two adjustable parameters; z the charge and b the repulsive interaction constant. Only the force constants and thus the dynamical matrix for the center-of-mass translations have been constructed. Therefore only branches with translational character are described by this model.

III. GROUP-THEORETICAL SELECTION RULES

The crystal structure of KN_3 is tetrahedral with space group D_{4h}^{18} (I_4/mcm). There are two molecules in the primitive cell. With respect to the tetragonal axis whose dimensions are a, a, and c, the potassium ions are located at 0, 0, $\frac{1}{4}$ and 0, 0, $\frac{3}{4}$ and the azide ions are at $\frac{1}{2}$, 0, 0 and 0, $\frac{1}{2}$, 0. The primitive lattice vectors have been previously described as have the projection operators for various symmetry directions and points in the Brillouin zone.[7] We wish to investigate the symmetry dependence of the neutron-scattering cross section for phonons in this structure.

Elliott and Thorpe[15] have given a systematic technique which can be used to derive the selection rules. The structure factor for those branches belonging to irreducible representation r for a momentum transfer $\vec{K}$ can be written in terms of the Elliot and Thorpe $\underline{B}$ matrix as

$$F_r(\vec{K}) = K^2 \textstyle\sum_s a_s'^2\, \tilde{\vec{L}} \cdot \underline{B}_s(r, \vec{q}) \cdot \vec{L} ,$$

where $\vec{L}$ is a unit column vector in the direction of $\vec{K}$, $\tilde{\vec{L}}$ is the transpose of $\vec{L}$ and

$$a_s' = a_s M_s^{-1/2} e^{-W_s(\vec{K})} .$$

Here, a_s, M_s, and $W_s(\vec{K})$ are, respectively, the scattering length, mass, and Debye-Waller factor of particles of type s.

In the present study only the LA and TA branches along the Λ $[0, 0, \mu]$ and Σ $[\mu, \mu, 0]$ lines were measured around reciprocal lattice points in the $(1\bar{1}0)$ plane.

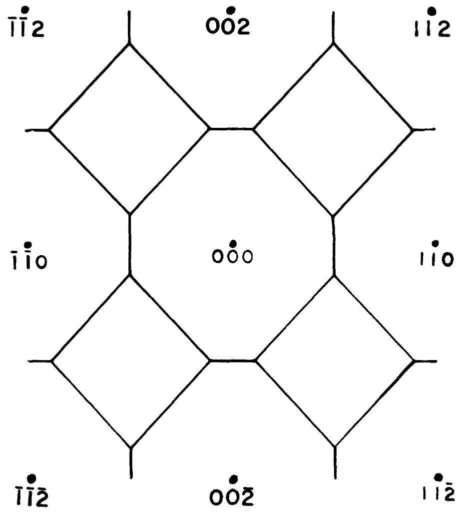

FIG. 2. Projection of the Brillouin zone on the $(1\bar{1}0)$ plane.

Figure 2 shows the projection of the Brillouin zone on the $(1\bar{1}0)$ plane. The $\underline{B}$ matrix is evaluated for the two values of $\vec{q}$ and the reciprocal lattice points which were used in the measurement. The resulting $\underline{B}$ matrices are shown in Table II. The transverse and longitudinal nature of the branches belonging to the several representations is clearly indicated by the $\underline{B}$ matrices.

In the case of the phonons along Λ, the $\underline{B}$ matrix for the potassium and nitrogen do not have the same form, that is, there are nonzero elements in the matrix for the nitrogen which are zero for potassium. This is due to the end nitrogen in the N_3^- ion which are not located at high symmetry positions. Considering the relative size of these elements, however, one can state that to a very good approximation the selection rules are determined by the large element in the $\underline{B}$ matrix. Thus, for the Λ phonon only those belonging to representation τ_1 and τ_5 are allowed, and for the Σ phonon only those belonging to the τ_1 and τ_4 representation are allowed. A knowledge of these facts greatly simplify the assignment of the observed neutron groups and, in particular, aids in the definite assignment of observed values to calculate phonons.

IV. EXPERIMENT

The measurements were performed with a standard triple-axis spectrometer mounted at the AMMRC reactor. The reactor is a light-water moderated 5 MW research reactor. The monochromator was a copper crystal whose (220) planes were used and the analyzer was an aluminum crystal whose (111) planes were used. The spectrometer was operated in both the constant Q (with the incident wavelength held fixed) and constant E modes, depending upon the slope of the dispersion curve. The sample was constructed of 26 crystals aligned with respect to each other and glued together. The aligning procedures that were used included both (a) the use of neutrons for those crystals whose morphology was inadequate and (b) optical methods for those crystals whose morphology allowed accurate determination of the zone axes. The resulting "crystal" exhibited a rocking curve of ~ 1.5°. Each of the component crystals was grown from a saturated water solution of the salt by slow evaporation. All the measurements were carried out at room temperature.

V. RESULTS AND DISCUSSION

Figure 3 presents the results of the measurements. The solid circles are the longitudinal modes and the solid triangles are the transverse modes as measured with neutrons. The solid lines are the results of the model calculations with the two parameters chosen as ($Z = 0.62$ and $b = 0.042 \times 10^{-12}$ erg). These parameters were obtained by fitting the acoustic modes along the line Λ. They are similar to those found for KBr ($Z = 0.7$ and b

TABLE II. Elliott and Thorps B matrix selection rules for neutron scattering.[a] (The notation is that of Ref. 7.)

Representation	K	$\vec{q} = [00\mu]\Lambda$ $\underline{B}$ Matrix	N
Reciprocal lattice point		(0, 0, 4)	(4, 4, 0) (4, 4, 2)
τ_1	$\begin{pmatrix}0&0&0\\0&0&0\\0&0&2\end{pmatrix}$	$\begin{pmatrix}0&0&0\\0&0&0\\0&0&6\end{pmatrix}$	$\begin{pmatrix}0.11&0.11&0\\0.11&0.11&0\\0&0&5.56\end{pmatrix}$
τ_2	$\underline{O}$	$\underline{O}$	$\begin{pmatrix}0.11&-0.11&0\\-0.11&0.11&0\\0&0&0\end{pmatrix}$
τ_3	$\underline{O}$	$\underline{O}$	$\begin{pmatrix}0.11&-0.11&0\\-0.11&0.11&0\\0&0&0\end{pmatrix}$
τ_4	$\underline{O}$	$\underline{O}$	$\begin{pmatrix}0.11&0.11&0\\0.11&0.11&0\\0&0&0.01\end{pmatrix}$
τ_5	$\begin{pmatrix}2&0&0\\0&2&0\\0&0&0\end{pmatrix}$	$\begin{pmatrix}6&0&0\\0&6&0\\0&0&0\end{pmatrix}$	$\begin{pmatrix}5.57&0&0\\0&5.57&0\\0&0&0.43\end{pmatrix}$

Representation	K	$\vec{q} = [\mu\mu 0]\Sigma$ $\underline{B}$ matrix	N
τ_1	$\begin{pmatrix}1&1&0\\1&1&0\\0&0&0\end{pmatrix}$		$\begin{pmatrix}3&3&0\\3&3&0\\0&0&0\end{pmatrix}$
τ_2	$\vec{O}$		$\vec{O}$
τ_3	$\begin{pmatrix}1&-1&0\\-1&1&0\\0&0&0\end{pmatrix}$		$\begin{pmatrix}3&-3&0\\-3&3&0\\0&0&0\end{pmatrix}$
τ_4	$\begin{pmatrix}0&0&0\\0&0&0\\0&0&2\end{pmatrix}$		$\begin{pmatrix}0&0&0\\0&0&0\\0&0&6\end{pmatrix}$

[a] The selection rules are valid for all reciprocal lattice points ($h\ h\ l$) except where noted.

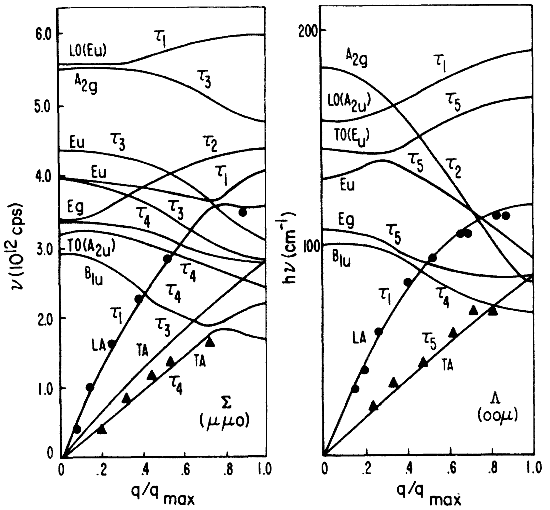

FIG. 3. Dispersion curves of KN_3 along the Σ and Λ directions. Solid circles are the longitudinal phonons and the solid triangles are the transverse phonon. Solid lines are the result of a model calculation as discussed in the text. Modes are labeled according to the irreducible representation to which they belong according to the notation of Ref. 7.

$= 0.03 \times 10^{-12}$ erg).[16] The dispersion curves are labeled according to the irreducible representation to which they belong. Use of the selection rules given in Table II allows very little ambiguity in the assignment of the observed phonon. Table I gives the results of the calculation of the infrared and Raman translational modes. The calculation adequately reproduces the neutron results but some of the infrared frequencies do not compare well. In view of the simplicity of the model, and the relatively limited amount of experimental data we did not feel justified in further attempts to improve the agreement. Rather, a model in which the rotation-translation coupling is not neglected and in which the charge distribution on the azide ion is more realistically included is being formulated. In addition, further neutron measurements in which the optical modes will be measured are planned. This latter step will, hopefully, indicate the effect of rotation-translation coupling by providing the true shape of the optical modes for comparison with those predicted by the present model.

ACKNOWLEDGMENTS

The authors would like to thank Professor Mitra for permission to quote his results on the infrared reflectance measurements prior to publication and would like to acknowledge many useful conversations with Dr. Russell Casella concerning the group-theoretical aspects of the work. One of us (K. R. R.) thanks the National Research Council, Washington, D. C., for the award of the NRC-FRL postdoctoral resident research associateship.

---

*NRC-FRL Postdoctoral Research Associate, now returned to Bhabha Atomic Research Centre, Trombay, India.

†Guests at Reactor Radiation Division, Natl. Bur. Std., Washington, D. C. 20234.

‡Present address: Department of Nuclear Engineering, Massachusetts Institute of Technology, Cambridge, Mass. 02139.

[1] S. Hendricks and L. Pauling, J. Am. Chem. Soc. 47, 2904 (1925).

[2] J. I. Bryant, J. Chem. Phys. 38, 2845 (1963).

[3] J. Govindarajan and T. M. Haridasan, Phys. Letters 28A, 701 (1969).

[4] Z. Iqbal, J. Chem. Phys. 53, 3763 (1970).

[5] C. E. Hathaway and P. A. Temple, Phys. Rev. (to be published).

[6] S. S. Mitra (private communication).

[7] K. R. Rao and S. F. Trevino, J. Chem. Phys. 53, 4661 (1970).

[8] E. W. Kellerman, Phil. Trans. Roy. Soc. London A238, 513 (1940).

[9] P. Gray and T. C. Waddington, Proc. Roy. Soc. (London) A235, 481 (1956).

[10] M. Born and K. Huang, *Dynamical Theory of Crystal Lattice* (Oxford U. P., London, 1954).

[11] G. Dolling, in *Molecular Dynamics and Structure of Solids*, edited by R. S. Carter and J. J. Rush, Natl. Bur. Std. (U.S.) Spec. Publ. No. 301 (U.S. GPO, Washington, D.C., 1969), p. 289.

[12] O. Schnepp and A. Ron, Discussions Faraday Soc. 48, 26 (1969).

[13] A. P. Roy and G. Venkataraman, Phys. Rev. 156, 769 (1967), and unpublished.

[14] L. Pauling, *The Nature of the Chemical Bond* (Cornell U. P., Ithaca, N. Y., 1960).

[15] R. J. Elliott and M. F. Thorpe, Proc. Phys. Soc. (London) 91, 903 (1967).

[16] H. Rafinzadeh, Ph. D. thesis (MIT, 1970) (unpublished).