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ELECTRONIC ENERGY BANDS IN POTASSIUM

TECHNICAL REPORT NO. 2

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DEPARTMENT OF PHYSICS

UNIVERSITY OF MIAMI

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Electronic Energy Bands in Potassium*

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(Abstract)

The method of orthogonalized plane waves is applied to a calculation of electronic energy levels in potassium, using a potential obtained from a self-consistent field. The energies of twenty-four states at four symmetry points in the Brillouin Zone have been obtained. The lowest band is dismissed in detail and the qualitative features of the density of states are presented. Departures from free electron bands are found. Comparison of higher bands with some other calculations suggests that certain features of band schemes may be reasonably independent of the potential used.

*Supported by the Office of Naval Research

1. INTRODUCTION

ELECTRONIC ENERGY LEVELS IN THE ALKALI METALS HAVE BEEN STUDIED FOR MANY YEARS. THE MAJORITY OF THE WORK HAS CONCERNED THE LIGHTER ELEMENTS, LITHIUM AND SODIUM[1].

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1. AN EXTENSIVE BIBLIOGRAPHY IS GIVEN BY J. S. SLATER, TECHNICAL REPORT NO. 4 OF THE SOLID STATE AND MOLECULAR THEORY GROUP, M.I.T., (1953), UNPUBLISHED.

PRINCIPAL ATTENTION HAS BEEN DEVOTED TO THE COHESIVE ENERGY AND TO RELATED PROPERTIES SUCH AS THE EQUILIBRIUM LATTICE CONSTANT AND THE COMPRESSIBILITY. THE HEAVIER ALKALI METALS: POTASSIUM, RUBIDIUM, AND CESIUM HAVE BEEN STUDIED LESS EXTENSIVELY[2 - 7].

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2. E. GORIN, PHYS. ZEITS. SOVJETUNION 9, 328 (1936).
3. T. S. KUHN AND J. H. VAN VLECK, PHYS. REV. 79, 382 (1950).
4. H. BROOKS, PHYS. REV. 91, 1027 (1953).
5. BERMAN, CALLAWAY, AND WOODS, PHYS. REV. 101, 1467 (1956).
6. F. S. HAM, SOLID STATE PHYSICS 1, 127 (1955).
7. R. M. STERNHEIMER, PHYS. REV. 78, 235 (1950).

THIS WORK HERE REPORTED CONCERNS AN APPLICATION OF THE METHOD OF ORTHOGONALIZED PLANE WAVES [8] TO A CALCULATION

8. C. HERRING, PHYS. REV. 57, 1169, (1940).

OF ELECTRONIC ENERGY BANDS IN POTASSIUM.

GORIN MADE A CALCULATION OF THE COHESIVE ENERGY OF POTASSIUM [2] USING THE CELLULAR METHOD [9 - 10] AND A

9. E. WIGNER AND F. SEITZ, PHYS. REV., 43, 804 (1933).

10. F. C. VON DER LAGE AND H. A. BETHE, PHYS. REV. 71, 612 (1947).

POTENTIAL OBTAINED FROM A SELF-CONSISTENT FIELD FOR THE K^+ ION. THE RESULTS OF HIS WORK WERE IN MARKED DISAGREEMENT WITH EXPERIMENT, IN THAT TOO LITTLE BINDING WAS OBTAINED. THIS FAILURE GAVE RISE TO THE BELIEF THAT AN ENERGY LEVEL CALCULATION BASED ON A SELF-CONSISTENT FIELD WOULD BE VERY INACCURATE FOR THE HEAVIER ALKALI METALS. THE QUANTUM DEFECT METHOD WAS DEVELOPED BY KUHN AND VAN VLECK [3] AND BY BROOKS [4] TO AVOID THIS DIFFICULTY BY USING OBSERVED SPECTROSCOPIC DATA TO CIRCUMVENT THE CONSTRUCTION OF AN EXPLICIT POTENTIAL. IT HAS RECENTLY BEEN SHOWN, HOWEVER, BY BERMAN, CALLAWAY AND WOODS [5] THAT IF PROPER ACCOUNT IS TAKEN OF EXCHANGE INTERACTIONS, A SELF-CONSISTENT FIELD METHOD CAN GIVE A RESULT OF REASONABLE ACCURACY FOR THE COHESIVE ENERGY

OF POTASSIUM. IT THEN BECOMES INTERESTING TO EXTEND THEIR WORK TO A CALCULATION OF HIGHER ELECTRONIC STATES.

IN MAKING THIS EXTENSION, THE METHOD OF ORTHOGONALIZED PLANE WAVES (OPW) WAS CHOSEN IN PREFERENCE TO THE CELLULAR METHOD BECAUSE IN THE OPW METHOD IT IS NOT NECESSARY TO SATISFY BOUNDARY CONDITIONS EXPLICITLY. THE PROBLEM OF ACCURATELY SATISFYING THE BOUNDARY CONDITIONS IS QUITE SERIOUS AND DIFFICULT IN THE CELLULAR METHOD[11], AND IT

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11. F. S. HAM, PH.D. THESIS, HARVARD UNIVERSITY (1954) (UNPUBLISHED).

WAS FELT THAT WITH THE CELLULAR METHOD, IT WOULD HAVE BEEN IMPRACTICAL TO STUDY MORE THAN A SMALL NUMBER OF ENERGY STATES. THE OPW METHOD HAS THE DISADVANTAGE THAT AN EXPLICIT POTENTIAL MUST BE USED, AND MORE IMPORTANT, THAT THE ELECTRON STATES IN THE ATOMIC CORE MUST BE KNOWN[12]. THERE ARE

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12. J. CALLAWAY, PHYS. REV. 97, 933, (1955).

REASONS WHY THE O.P.W. METHOD SHOULD BE EXPECTED TO WORK WELL FOR METALLIC POTASSIUM. AS IN THE OTHER ALKALI METALS, ONE HAS ONE ELECTRON MOVING OUTSIDE OF A RELATIVELY COMPACT ION CORE. CONSEQUENTLY, OVERLAPING OF CORE WAVE FUNCTIONS WILL BE NEGLIGIBLE. THE SELF-CONSISTENCY PROBLEM, ALSO, SHOULD NOT BE SERIOUS SINCE IT IS REASONABLE TO EXPECT THAT THE AVERAGE DISTRIBUTION OF ELECTRONS IN THE CORE SHOULD NOT BE SIGNIFICANTLY AFFECTED BY THE VALENCE ELECTRON. THIS IS

SUPPORTED BY A CALCULATION OF HARTREE AND HARTREE FOR THE K^+ ION IN WHICH IT WAS FOUND THAT THE WAVE FUNCTION OF THE 3_p ELECTRON DIFFERED ONLY SLIGHTLY FROM THAT FOR THE K^+ ION[13].

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13. D. R. HARTREE AND W. HARTREE, PROC. CAMBRIDGE PHIL. SOC. 34, 550 (1938).

THE APPROXIMATION OF WIGNER AND SEITZ IS ALSO MADE: THAT THERE IS ONLY ONE VALENCE ELECTRON IN AN ATOMIC CELL WHICH MOVES IN THE POTENTIAL OF THE POSITIVE ION, ALL OTHER CELLS BEING NEUTRAL. THE CRYSTAL POTENTIAL AND CORE WAVE FUNCTIONS USED HERE WERE OBTAINED FROM A SELF-CONSISTENT FIELD WITH EXCHANGE FOR THE K^+ ION[14].

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14. D. R. HARTREE AND W. HARTREE, PROC. ROYAL SOCIETY, 166A, 450 (1936).

BECAUSE OF THE SIMPLICITY OF THE PHYSICAL SITUATION POTASSIUM SHOULD BE A VERY FAVORABLE SYSTEM FOR AN ENERGY BAND STUDY. SUCH A STUDY SHOULD FURNISH INFORMATION CONCERNING: (1) VALIDITY OF THE FREE ELECTRON APPROXIMATION. THERE ARE THREE ASPECTS HERE: (A) DEPARTURES OF EFFECTIVE MASS VALUES FROM 1, (B) PRESENCE OF K^4 AND HIGHER TERMS IN THE E(K) EXPANSION AND (C) DEPARTURES OF ENERGY SURFACES FROM SPHERICAL SYMMETRY. ONE MIGHT EXPECT THAT THESE EFFECTS WOULD BE MORE PRONOUNCED FOR EXCITED LEVELS RATHER THAN FOR THE LOWEST BAND. (2) COMPARISON OF ENERGY BANDS IN POTASSIUM

WITH THOSE CALCULATED FOR OTHER ELEMENTS HAVING THE BODY CENTERED CUBIC STRUCTURE: ONE OF THE MOST IMPORTANT PROBLEMS IN ENERGY BAND THEORY IS THE QUESTION OF HOW SENSITIVE IS THE BAND STRUCTURE TO DETAILS OF THE POTENTIAL. COMPARISON OF ENERGY BANDS IN DIFFERENT ELEMENTS OF THE SAME CRYSTAL STRUCTURE SHOULD FURNISH INFORMATION ON THIS QUESTION. IN ADDITION, THE EFFECT OF CHANGES IN THE POTENTIAL ON THE BANDS IN POTASSIUM CAN ALSO BE EXAMINED.

UNFORTUNATELY, THERE IS A DEARTH OF ACCURATE EXPERIMENTAL EVIDENCE PERTAINING TO ENERGY BANDS IN POTASSIUM, SO THAT A DETAILED COMPARISON OF THEORY AND EXPERIMENT IS NOT POSSIBLE. QUALITATIVE COMPARISONS AND PREDICTIONS CAN BE MADE IN SOME CASES. IT IS HOPED THIS THEORETICAL DISCUSSION WILL STIMULATE EXPERIMENTAL EFFORT.

II. THE CRYSTAL POTENTIAL

WE ASSUME THAT EACH ELECTRON EXPERIENCES ONLY THE POTENTIAL OF THE CORRESPONDING POSITIVE ION. THIS POTENTIAL CONSISTS OF TWO PARTS: (1) THE COULOMB POTENTIAL OF THE ATOMIC NUCLEUS AND THE AVERAGE DISTRIBUTION OF THE CORE ELECTRONS, AND (2) THE EXCHANGE INTERACTION BETWEEN THE VALENCE ELECTRONS AND THE CORE. THE COULOMB POTENTIAL IS OBTAINED IN THE OBVIOUS WAY FROM THE CORE ELECTRON DISTRIBUTION. THE EXCHANGE INTERACTION IS APPARENTLY QUITE IMPORTANT IN OBTAINING NUMERICAL RESULTS IN A COHESIVE ENERGY CALCULATION.

WE CAN DEFINE AN EFFECTIVE EXCHANGE POTENTIAL FOR THE STATE $\psi^{i}_{\underline{K}}$ (i'TH IRREDUCIBLE REPRESENTATION OF WAVE VECTOR $\underline{K}$) IN THE FOLLOWING WAY:

$$V^{i}_{\underline{K}}(R_1) = \frac{\sum_{NLM} \left[\int \psi^{*}_{NLM}(R_2)^{2} / R_{12} \; \psi^{i}_{\underline{K}}(R_2)\, dR_2 \right] \psi_{NLM}(R_1)}{\psi^{i}_{\underline{K}}(R_1)} \qquad (1)$$

WHERE ψ_{NLM} REPRESENTS A CORE WAVE FUNCTION. THE EXCHANGE POTENTIAL COMPUTED ACCORDING TO (1) WILL DIFFER FROM STATE TO STATE, AND OBVIOUSLY DEPENDS ON THE WAVE FUNCTION OF THE STATE CONSIDERED. THIS MEANS THAT A SELF-CONSISTENT SOLUTION OF THE HARTREE-FOCK EQUATION IS REQUIRED. SLATER HAS PROPOSED TWO METHODS OF AVERAGING THE EXCHANGE POTENTIAL[15]

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15. J. C. SLATER, PHYS. REV., 81, 385 (1951).

WHICH ALLOW ONE TO USE ONE EXCHANGE POTENTIAL FOR ALL STATES. IT IS DOUBTFUL THAT SUCH A PROCEDURE WILL HAVE QUANTITATIVE SUCCESS [16], [17].

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16. HERMAN, CALLAWAY, AND ACTON, PHYS. REV. 95, 371, (1954).

17. J. CALLAWAY, PHYS. REV., 99, 500 (1955).

A MORE ACCURATE PROCEDURE WOULD BE TO ASSUME THE EXCHANGE POTENTIAL FOR A GIVEN STATE DEPENDS PRIMARILY ON THE ANGULAR

MOMENTUM OF THE STATE CONSIDERED, OR IN THE CASE OF THE SOLID, ON THE PREDOMINANT ANGULAR MOMENTUM IN THE DECOMPOSITION OF $\psi^{i}_{\underline{k}}$ INTO SPHERICAL HARMONICS[16]. IN OBTAINING THE EXCHANGE POTENTIAL FOR A STATE OF ANGULAR MOMENTUM L, OF A VALENCE ELECTRON, IT IS QUESTIONABLE WHETHER IT IS DESIRABLE TO AVERAGE THE EXCHANGE POTENTIALS OF THE CORE ELECTRON STATES OF ANGULAR MOMENTUM L, SINCE THESE HAVE ENERGY VALUES IN GENERAL FAR BELOW THAT OF THE STATE WE ARE CONSIDERING. IT SEEMS MORE REASONABLE TO CONSTRUCT AN EXCHANGE POTENTIAL FOR A GIVEN L FROM AN APPROXIMATE WAVE FUNCTION FOR A VALENCE ELECTRON STATE OF THAT L.

SUCH A PROCEDURE WAS FOLLOWED IN THIS CALCULATION. AN S STATE EXCHANGE POTENTIAL WAS CONSTRUCTED FROM THE SELF-CONSISTENT FIELD CORE WAVE FUNCTIONS AND THE LOWEST ORTHOGONALIZED PLANE WAVE FOR THE STATE Γ_1. THIS POTENTIAL WAS USED FOR THE STATES Γ_1, H_1, P_1, AND N_1. IT IS TO BE NOTED THAT THE STATE N_1 WILL CONTAIN AN ADMIXTURE OF D FUNCTIONS. A P STATE EXCHANGE POTENTIAL WAS SIMILARLY OBTAINED FROM THE LOWEST O.P.W. FOR THE STATE H_{15}, AND USED IN THE CALCULATIONS FOR Γ_{15}, H_{15}, P_4, N_1' N_3', N_4'. P_4 WILL ALSO HAVE SOME D CHARACTER. A D STATE EXCHANGE POTENTIAL WAS OBTAINED FROM A D FUNCTION CALCULATED WITHOUT EXCHANGE IN A PRIOR CALCULATION OF K^4 TERMS IN THE E ($\underline{K}$) RELATION. THIS POTENTIAL WAS USED FOR THE D-LIKE STATES Γ_{25}, Γ_{12}, H_{25}, H_{12}, P_3, N_2, N_3, N_4, AND ALSO FOR THE F LIKE STATES Γ_{25}, $\Gamma_{2'}$, H_{25}, $H_{2'}$, P_5 AND $N_{2'}$. IT WAS ASSUMED IN USING THE O.P.W. METHOD THAT THE CORE STATES COULD WITH

SUFFICIENT ACCURACY, BE CONSIDERED AS EIGENFUNCTION IN THESE POTENTIALS.

ONE UNSATISFACTORY FEATURE OF THIS PROCEDURE IS THAT IN THE CASE OF THE S AND P STATES THE EXCHANGE POTENTIAL ACCORDING TO (1) WILL HAVE INFINITIES WHERE THE APPROXIMATE $\psi^{i}_{\underline{K}}$ HAS ZEROS. THESE WERE REMOVED IN SUCH A WAY AS TO GIVE A REASONABLY SMOOTH EXCHANGE POTENTIAL. THE COULOMB POTENTIAL AND THE POTENTIAL FOR S, P, AND D STATES ARE TABULATED IN TABLE 1. CERTAIN IRREGULARITIES MAY BE NOTED IN THE QUANTITIES RV_s AND RV_p IN THE NEIGHBORHOOD OF R=2. THESE RESULT FROM THE METHOD OF TREATING THE EXCHANGE POTENTIAL NEAR A SINGULARITY. SINCE THESE IRREGULARITIES OCCUR IN A REGION IN WHICH THE WAVE FUNCTION IS SMALL, THE EFFECT ON THE ENERGY SHOULD NOT BE LARGE.

III. CALCULATION OF THE ENERGY LEVELS

THE O.P.W. METHOD LEADS TO A SECULAR EQUATION OF THE FORM

$$\text{DET} \left[(X_{\underline{K}}, H X_{\underline{H}}) - E(X_{\underline{K}}, X_{\underline{H}}) \right] = 0 \qquad (2)$$

WHERE H IS THE CRYSTAL HAMILTONIAN AND $X_{\underline{K}}$ IS AN ORTHOGONALIZED PLANE WAVE:

$$X_{\underline{K}} = e^{i\,\underline{K}\cdot\underline{R}} - \Sigma_J \Sigma_\nu \mu_{\underline{K}\,J}\, e^{i\underline{K}\cdot\underline{R}_\nu}\, \phi_J\,(\underline{R}-\underline{R}_\nu) \qquad (3)$$

HERE ϕ_J IS A CORE FUNCTION FOR THE CORE STATE J, R_2 IS A LATTICE VECTOR AND $\mu_{\underline{K}J} = \frac{1}{\Omega_0^{1/2}} \int \phi_J^{+}(r)\, e^{i\underline{K}\cdot\underline{r}}\, d\underline{r}$ WITH Ω_0 = THE VOLUME OF THE ATOMIC CELL (13).

18. THIS CALCULATION WAS MADE FOR A LATTICE PARAMETER OF 5.20A°, OR R_s=4.84 ATOMIC UNITS.

IN PRACTICE WE USE LINEAR COMBINATIONS OF ORTHOGONALIZED PLANE WAVES WHICH TRANSFORM ACCORDING TO PARTICULAR IRREDUCIBLE REPRESENTATIONS IN SETTING UP (2).

WE ASSUME THAT THE CORE STATES ϕ_J ARE EIGENFUNCTIONS OF THE CRYSTAL HAMILTONIAN. IN THIS CASE, THE MATRIX ELEMENTS IN (2) ARE

$$(X_K, HX_H) = K^2 \delta_{KH} + V(\underline{K}-\underline{H}) - \Sigma_J E_J \mu^*_{KJ} \mu_{HJ} \qquad (4)$$

AND

$$(X_K, X_H) = \delta_{KH} - \Sigma_J \mu_{KJ}^* \mu_{HJ}$$

WHERE E_J IS THE ENERGY VALUE OF THE CORE STATE J AND $V(\underline{K})$ IS A FOURIER COEFFICIENT OF POTENTIAL

$$V(K) \quad \int e^{iK\cdot R} \; V(\underline{R}) \, d\underline{R} \qquad (5)$$

THE FOURIER COEFFICIENTS $V(K)$ ARE GIVEN IN A TABLE (2) AS FUNCTIONS OF $M^2 = (\frac{A}{2\pi} \underline{K})^2$ FOR S, P AND D STATES (A IS THE LATTICE PARAMETER).

IN CONNECTION WITH THE FOURIER COEFFICIENTS, BUTCHER (13)

13. P. N. BUTCHER, PROC. PHYS. SOC. 64A, 765 (1951).

HAS OBTAINED $V(M^2=2)$ FOR POTASSIUM AND SEVERAL OF THE OTHER ALKALI METALS FROM A DISCUSSION OF THE OPTICAL PROPERTIES

BASED ON THE APPROXIMATION OF NEARLY FREE ELECTRONS. H IS VALUE OF 0.305 E.V. SEEMS TO BE TOO SMALL BY NEARLY AN ORDER OF MAGNITUDE. THIS IS PROBABLY DUE TO FAILURE OF THE APPROXIMATION OF NEARLY FREE ELECTRONS.

O.P.W. EXPANSIONS WERE CONSTRUCTED FOR 24 STATES MENTIONED IN SECT. II AT THE SYMMETRY POINTS Γ, H, P, AND N IN THE BRILLOUIN ZONE. THE BRILLOUIN ZONE FOR THE BODY CENTERED CUBIC LATTICE IS SHOWN IN FIGURE 1. LINEAR COMBINATIONS OF ORTHOGONALIZED PLANE WAVES WERE EMPLOYED WHICH TRANSFORMED ACCORDING TO THE IRREDUCIBLE REPRESENTATIONS OF INTEREST (SEE APPENDIX OF REFERENCE 17). BECAUSE HIGH SPEED ELECTRONIC COMPUTING EQUIPMENT IS NOT AVAILABLE AT THE UNIVERSITY OF MIAMI, THE COMPUTATIONS DID NOT IN GENERAL INVOLVE HIGHER THAN FOURTH ORDER DETERMINANTS. FIFTH ORDER DETERMINANTS WERE SOLVED FOR TWO STATES: N_1 AND P_4. THIRD AND SECOND ORDER DETERMINANTS WERE USED FOR THE STATES IN THE F BAND WHERE ONLY A QUALITATIVE INDICATION OF THE ENERGY IS REQUIRED. SUCH HIGHLY EXCITED STATES CAN PROBABLY BE REASONABLY WELL REPRESENTED BY SMALL NUMBERS OF PLANE WAVES. THE LOWEST TWO EIGENVALUES, (IN ONE CASE, THREE) OF ALL THE REPRESENTATIONS CALCULATED ARE GIVEN IN TABLE 3. THE ORDER OF THE LEVELS AT THE FOUR SYMMETRY POINTS IS SHOWN IN FIGURE 2.

IN ORDER TO STUDY THE CONVERGENCE OF THE O.P.W. EXPANSION, AN EIGHTH ORDER SECULAR DETERMINANT FOR THE STATE Γ_1 WAS SOLVED ON THE WHIRLWIND COMPUTER AT THE MASSACHUSETTS

INSTITUTE OF TECHNOLOGY THROUGH THE COURTESY OF PROFESSOR J. C. SLATER AND MR. F. J. CORBATO. CONVERGENCE OF THE EIGENVALUE TO THE VALUE -.447 FOUND BY THE CELLULAR METHOD FOR THIS STATE FOR THE POTENTIAL V_s APPEARED TO BE SLOW. (THE BEST VALUE OF THE ENERGY OF THE LOWEST STATE IS -.453 RYDBERGS FOUND FROM THE HARTREE-FOCK EQUATIONS DIRECTLY WITHOUT THE APPROXIMATION OF AN EXCHANGE POTENTIAL.) TABLE 4 SHOWS THE LOWEST EIGENVALUE IN EACH ORDER: FROM FIRST TO EIGHTH, AND THE LOWEST SIX EIGENVALUES IN EIGHTH ORDER. IT IS INTERESTING TO NOTE THAT THE MAJOR CHANGE OCCURS BETWEEN FIRST AND SECOND ORDER (WHERE THERE ARE 13 WAVES). THERE ALSO SEEMS TO BE A CLUSTERING OF EIGENVALUES IN A REGION NEAR $E=+1.25$. A SMALL EIGENVALUE CHANGE IN EACH ORDER IS NECESSARY, BUT NOT SUFFICIENT TO ENSURE CONVERGENCE.

USING THIS EXAMPLE AS A GUIDE, WE WOULD EXPECT THAT THOSE SOLUTIONS OF FOURTH ORDER DETERMINANTS BASED ON FORTY OR MORE WAVES SHOULD BE CONVERGENT TO ABOUT 0.04 RYDBERG. THIS ESTIMATE MAY BE CONSERVATIVE, FOR SOME OF THE HIGHER STATES MAY BE BETTER REPRESENTED BY A FEW ORTHOGONALIZED PLANE WAVES THAN THIS STATE. IN PARTICULAR, THE CONVERGENCE OF THE D BAND STATES MAY BE SOMEWHAT BETTER. IT IS ALSO REASONABLE TO EXPECT THAT THE DIFFERENCES BETWEEN ENERGY LEVELS FOUND USING APPROXIMATELY THE SAME NUMBER OF WAVES IS STABLE. FOR THIS REASON, IT IS LIKELY THAT THE STATE N_1 WILL CONTINUE TO LIE BELOW N_1'. HOWEVER, IT IS POSSIBLE THAT IN HIGHER ORDER, P_4 WOULD BE FOUND TO LIE BELOW H_{12},

SINCE H_{12} APPEARS NEARLY CONVERGENT IN FOURTH ORDER WITH 54 WAVES WHILE P_4 IS FARTHER FROM CONVERGENT IN FIFTH ORDER WITH 24 WAVES. (BY A PECULIARITY OF THE GROUP THEORY, EACH ORDER OF THE SECULAR DETERMINANT FOR P_4 ONLY INCLUDES A SMALL NUMBER OF ADDITIONAL WAVES.) MANY OF THE RESULTS OF THIS WORK DEPEND ONLY ON RELATIVE POSITIONS OF THE LEVELS AND ARE PROBABLY RELIABLE EVEN IF THE ABSOLUTE VALUE OF THE ENERGIES ARE SOMEWHAT UNCERTAIN. NEVERTHELESS, THE CONVERGENCE APPEARS TO BE MUCH POORER THAN THAT OF THE AUGMENTED PLANE WAVE METHOD[20].

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20. D. J. HOWARTH, PHYS. REV. 99, 469 (1955).

A VERY IMPORTANT QUESTION IN THE CALCULATION OF ENERGY BANDS IS THE SENSITIVITY OF THE ELECTRON ENERGY LEVELS TO CHANGES IN THE POTENTIAL. ONE WOULD HOPE THAT SUCH FEATURES AS THE RELATIVE ORDER OF THE LEVELS AT A SYMMETRY POINT WOULD BE REASONABLY INDEPENDENT OF DETAILS OF THE POTENTIAL. UNFORTUNATELY, THE CONTRARY RESULT SEEMS TO BE INDICATED BY SOME WORK OF HOWARTH[20]. HOWARTH FOUND THAT THE ASSUMPTION THAT THE POTENTIAL IS CONSTANT IN THE REGION OUTSIDE THE INSCRIBED SPHERE IN THE ATOMIC CELL WAS SUFFICIENT TO INVERT THE TRIPLY DEGENERATE AND DOUBLY DEGENERATE D-BAND LEVELS AT THE CENTER OF THE BRILLOUIN ZONE IN COMPARISON TO AN EARLIER CALCULATION.[21]. THIS MODIFICATION OF THE POTENTIAL IS USED

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21. K. J. HOWARTH, PROC. ROY. SOC. (LONDON) A220 513 (1953).

NOT ONLY IN THE AUGMENTED PLANE WAVE METHOD EMPLOYED BY HOWARTH[14] BUT ALSO IN THE METHOD OF KOHN AND ROSTOKER[22].

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22. W. KOHN AND N. ROSTOKER, PHYS. REV. 94, 1111, (1954).

THE EFFECT OF SUCH A MODIFICATION OF THE POTENTIAL WAS EXAMINED IN THIS CASE. SINCE THE CORE WAVE FUNCTIONS DO NOT EXTEND INTO THE REGION IN WHICH THE POTENTIAL IS TO BE MODIFIED, IT IS NECESSARY ONLY TO CONSIDER THE EFFECT OF APPROPRIATE CHANGES IN THE FOURIER COEFFICIENTS OF POTENTIAL. TO SUFFICIENT ACCURACY, WE MAY ASSUME THAT THE ORIGINAL POTENTIAL IS JUST THE COULOMB POTENTIAL $^{2}/_{R}$ OF THE POSITIVE ION. IT IS ADVANTAGEOUS TO CHOOSE THE CONSTANT POTENTIAL SO THAT THE $M^2=0$ COEFFICIENT OF THE DIFFERENCE VANISHES. SINCE THE COULOMB POTENTIAL IS REASONABLY FLAT IN THIS REGION, THE DIFFERENCE IN THE POTENTIALS IS SMALL, AND THE FOURIER COEFFICIENTS OF THE DIFFERENCE IN POTENTIAL (WHICH MAY BE COMPUTED ANALYTICALLY) ARE SO SMALL THAT THE EFFECTS ON THE ENERGY LEVELS ARE QUITE NEGLIGIBLE. THERE MAY, HOWEVER, BE GOOD REASON WHY THIS MODIFICATION IS NOT SO SERIOUS AS IN HOWARTH'S CASE[20].

IV. DEPARTURES FROM THE EFFECTIVE MASS APPROXIMATION

THE EFFECTIVE MASS NEAR $K=0$ CAN BE TAKEN FROM THE WORK OF BERMAN, CALLAWAY AND WOODS AS 85.6 PER CENT OF THE FREE ELECTRON MASS. HOWEVER, THE PROXIMITY OF D BAND STATES AT N, H, AND P TO THE GROUND STATE Γ_1 (NOTE THAT N_1, AND P_4 CONTAIN D FUNCTIONS AS WELL AS S AND P RESPECTIVELY) SUGGEST

THAT THERE MAY BE APPRECIABLE K^4 TERMS IN THE EXPANSION OF E ($\underline{K}$) NEAR $\underline{K}$=0. THE COEFFICIENT OF K^4 CAN BE CALCULATED ACCORDING TO THE PROCEDURE OF SILVERMAN[23] WITHIN

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23. R. A. SILVERMAN, PHYS. REV. 85, 227 (1952).

THE FRAMEWORK OF THE CELLULAR METHOD.

ACCORDING TO SILVERMAN, IF WE WRITE

$$E(K) = E_0 + E_2 K^2 + E_4 K^4 \tag{6}$$

THEN

$$E_4 = \frac{2}{5} R_s^2 E_2 - \frac{4}{15} \frac{E_2^2}{\gamma} R_s^2 \left(R f_D' / f_D'\right)^{-1} + \frac{\gamma E_2}{u_0(R_s)} \left[\frac{1}{\gamma} E_2 \left(\frac{\partial u_0}{\partial E}\right)_{R_s, E_0} - R_s u_0(R_s) \frac{\int_0^{R_s} P_p^2 \, DN}{P_p^2(R_s)} \right] \tag{7}$$

WHERE R_s IS THE RADIUS OF THE ATOMIC SPHERE,

$$\gamma = \frac{R_s^3 u_0^2(R_s)}{3},$$

u_0 IS THE CELLULAR METHOD WAVE FUNCTION FOR K=0, f_D IS A SOLUTION OF THE WAVE EQUATION FOR A D STATE OF ENERGY E_0, AND P_p IS THE P FUNCTION INVOLVED IN THE USUAL CALCULATION OF THE EFFECTIVE MASS. THIS EXPRESSION WAS EVALUATED USING THE RESULTS FOR u_0, E_0, E_2, AND P_p OF THE PREVIOUS CALCULATION OF BERMAN, CALLAWAY AND WOODS[5] PLUS A D FUNCTION CALCULATED USING THE POTENTIAL V_D GIVEN IN TABLE I

FOR ENERGY E_0. THE QUANTITY $\left(\frac{\partial u_0}{\partial E}\right)_{R_s, E0}$ WAS EVALUATED BY EXPRESSING U_0 FOR $R>4$ AS A SUM OF REGULAR AND IRREGULAR COULOMB FUNCTIONS WITH COEFFICIENTS THAT ARE KNOWN FUNCTIONS OF ENERGY ACCORDING TO THE PROCEDURE OF HAM[24] AND THEN

24. F. S. HAM, ONR TECHNICAL REPORT NO. 204, CRUFT LABORATORY, HARVARD UNIVERSITY, (1954) (UNPUBLISHED).

DIFFERENTIATING THE EXPANSION. THE VALUE OF E_4 OBTAINED WAS 1.64 IN ATOMIC UNITS. SUCH A TERM WOULD GIVE A CONTRIBUTION TO THE COHESIVE ENERGY IN THE CELLULAR METHOD OF $\frac{5.81E_4}{R_s^{\,4}}$ OR 5.4 K-CAL/MOL (A REPULSION), WHICH, HOWEVER, IS PROBABLY CANCELLED BY THE ADDITIONAL ATTRACTIONS RESULTING FROM POLARIZATION AND RELATIVISTIC EFFECTS.

THIS RELATIVELY LARGE VALUE OF E_4 INDICATES THAT THERE WILL BE MARKED DEVIATIONS OF THE ENERGY SURFACES FROM THE FREE ELECTRON APPROXIMATION. AS POINTED OUT BY DR. M. H. COHEN[25], A LARGE E_4 ALSO SUGGESTS THAT THERE MAY BE

25. M. H. COHEN, PRIVATE COMMUNICATION.

IMPORTANT DEVIATIONS OF THE ENERGY SURFACES FROM SPHERICAL SYMMETRY, SINCE IF EXPANDED IN POWERS OF $\underline{K}$, THE LOWEST SUCH TERMS WILL BE PROPORTIONAL TO THE FOURTH POWER OF THE WAVE VECTOR.

V. STRUCTURE OF THE LOWEST BAND

IN ORDER TO DETERMINE THE FORM OF THE LOWEST $E(\underline{k})$ SURFACE, IT IS NECESSARY TO DETERMINE THE ENERGIES OF A LARGE NUMBER OF THE STATES BETWEEN THE END POINTS Γ_1 AND H_{12} OF THE BAND. THIS IS VERY DIFFICULT BECAUSE A VERY LARGE NUMBER OF TERMS IN THE O.P.W. SECULAR DETERMINANT WOULD BE REQUIRED IN ORDER TO INCLUDE A REASONABLE NUMBER OF WAVES, EVEN ALONG SYMMETRY AXES LIKE $\Delta(100)$. ACCORDINGLY, WE HAVE RECOURSE TO AN INTERPOLATION SCHEME. IT SEEMS NATURAL TO EXPAND $E(\underline{k})$ IN A FOURIER SERIES, INCLUDING ONLY THOSE TERMS WHICH HAVE THE PROPER SYMMETRY. AN EXPANSION IN POWERS OF K, I.E., KUBIC HARMONICS, ABOUT K=0 DOES NOT SEEM DESIRABLE BECAUSE IT WILL BE DIFFICULT TO OBTAIN THE PROPER BEHAVIOR OF $E(\underline{k})$ AT SYMMETRY POINTS. THE FOURIER SERIES APPROACH MEETS THIS REQUIREMENT. IF WE CONSIDER THE LOWEST PLANE WAVES THAT ARE PERIODIC IN THE RECIPROCAL LATTICE, WE HAVE

$$
\begin{aligned}
E(\underline{k}) = E_0 &+ \cos\xi \cos\eta \cos\zeta + \beta(\cos 2\xi + \cos 2\eta + \cos 2\zeta) \\
&+ \gamma(\cos 2\xi \cos 2\eta + \cos 2\xi \cos 2\zeta + \cos 2\eta \cos 2\zeta \\
&+ (\cos 3\xi \cos\eta \cos\zeta + \cos 3\eta \cos\xi \cos\zeta + \cos 3\zeta \cos\eta \cos\xi)
\end{aligned}
\tag{8}
$$

WHERE $\xi = K_x A$, ETC.).

SUCH AN EXPANSION WILL HAVE THE PROPER ZERO GRADIENT AT SYMMETRY POINTS. THIS IS, IN FACT, JUST THE FORM OF EXPRESSION FOR A SINGLE S BAND THAT IS OBTAINED FROM THE TIGHT BINDING INTERPOLATION SCHEME OF SLATER AND KOSTER[26].

26. J. C. SLATER AND G. F. KOSTER, PHYS. REV. 94, 1048 (1954)

AN ATTEMPT WAS MADE TO FIT THE LOWEST BAND WITH AN EXPRESSION OF THIS FORM. A FIVE PARAMETER SCHEME WAS CHOSEN USING E_0, α, β, γ, δ AS IN (8). THE CONSTANTS WERE DETERMINED FROM THE ENERGY OF THE Γ_1 STATE (E_{Γ_1} = -.4525) AND THE EFFECTIVE MASS NEAR K=0 TAKEN FROM THE CALCULATION OF BERMAN, CALLAWAY AND WOODS ($E_2 = M/M^* = 1.168$)(5), AND THE LOWEST ENERGIES OF THE STATES H_1, P_4, AND N_1. THE CONSTANTS ARE GIVEN IN TABLE V.

TABLE V

PARAMETERS IN EQUATION (8)

E_0	=	-.2410
α	=	-.1057
β	=	-.0277
γ	=	+.0306
δ	=	+.0172

THE ENERGY BANDS DETERMINED BY EQUATION (8) ARE SHOWN IN FIGURES 3 AND 4, FOR THE 00 AND 110 AXES, WHERE THEY ARE COMPARED WITH THE PARABOLIC BANDS FOR "FREE ELECTRONS" WITH AN EFFECTIVE MASS RATIO $M/M^* = 1.168$.

THE BANDS SHOWN IN FIGURES 3 AND 4 DEVIATE IN IMPORTANT RESPECTS FROM THE FREE ELECTRON APPROXIMATION. IT IS LIKELY THAT THESE DEVIATIONS ARE TOO LARGE, SINCE IF E_4 IS CALCULATED FROM (8), IT TURNS OUT TO BE CONSIDERABLY LARGER, THOUGH OF THE SAME SIGN, THAN THAT FOUND FROM THE CELLULAR METHOD. IT IS NOT EASY TO FIT A SPHERICAL FREE ELECTRON BAND ACCURATELY IN THIS WAY. HOWEVER, THE QUALITATIVE FEATURES MAY BE CORRECT. THE BANDS FIRST RISE SOMEWHAT FASTER THAN THE FREE ELECTRON APPROXIMATION INDICATES AND THEN LEVEL OFF SO AS TO HAVE ZERO SLOPE COMING INTO H AND N.

IT WAS BELIEVED THAT ACCURACY OF EQUATION (8) WITH THE FIVE PARAMETERS GIVEN WAS NOT SUFFICIENT TO JUSTIFY A DETAILED AND ACCURATE CALCULATION OF THE DENSITY OF STATES. THE NUMERICAL CALCULATION OF A DENSITY OF STATES FROM (8) WOULD HAVE TO BE DONE VERY CAREFULLY SINCE WE ARE LOOKING FOR DEVIATION FROM THE $\sqrt{E - E_{\Gamma_1}}$ BEHAVIOR OF A FREE ELECTRON BAND. IN ORDER TO GET SOME INSIGHT INTO THE QUALITATIVE FEATURES OF THE DENSITY OF STATES CURVE, IT IS PROBABLY SUFFICIENTLY ACCURATE TO USE THE METHOD OF HOUSTON (27) IN WHICH THE DENSITY OF

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27. W. V. HOUSTON, REV. MOD. PHYS. 20, 161 (1948).

STATES CURVE IS COMPUTED ALONG CERTAIN SYMMETRY LINES IN THE BRILLOUIN ZONE, AND THE OVER ALL DENSITY OF STATES IS FOUND BY INTERPOLATION. HOUSTON'S METHOD IS KNOWN TO GIVE USE TO SPURIOUS SINGULARITIES RESULTING FROM EXAGGERATED CONTRIBUTIONS FROM SYMMETRY POINTS SUCH AS N, H, AND P WHERE THE ENERGY SURFACES HAVE ZERO GRADIENT. BUT THE OCCUPIED PORTION OF THE BAND, WITH WHICH WE ARE PRIMARILY CONCERNED, DOES NOT EXTEND UP TO N, WHICH IS THE CRITICAL POINT CLOSEST TO THE ORIGIN. CONSEQUENTLY, HOUSTON'S METHOD WILL GIVE NO SPURIOUS SINGULARITIES IN THE OCCUPIED PORTION OF THE DENSITY OF STATES CURVE.

A QUALITATIVE DENSITY OF STATES CURVE IS SHOWN IN FIGURE 5 WHERE IT IS COMPARED WITH THAT FOR A PARABOLIC BAND. FOR ENERGIES ONLY SLIGHTLY ABOVE THE BOTTOM OF THE BAND, THE DENSITY OF STATES CURVE MUST COINCIDE WITH THAT FOR A FREE ELECTRON BAND, SINCE ONE OF THE CONDITIONS ON EQUATION (8) WAS THAT IT YIELD THE CORRECT EFFECTIVE MASS. AS THE ENERGY INCREASES, THE PHYSICAL CURVE RISES MORE SLOWLY THAN THE FREE ELECTRON CURVE DUE TO THE EFFECT OF THE POSITIVE K^4 TERMS. BUT AS THE ENERGY RISES STILL FURTHER, THE BAND FLATTENS, AND THE DENSITY OF STATES CURVE CROSSES THE FREE ELECTRON CURVE. THIS CROSS-OVER HAS PROBABLY OCCURRED BEFORE THE FERMI SURFACE IS REACHED,

SO THAT THE DENSITY OF STATES ON THE FERMI SURFACE SHOULD BE HIGHER THAN FOR A FREE ELECTRON GAS. ONE WOULD ALSO EXPECT DEVIATIONS FROM SPHERICAL SYMMETRY.

BEYOND THE FERMI LEVEL, THE DENSITY OF STATES SHOULD RISE RAPIDLY TO A PEAK AT AN ENERGY IN THE NEIGHBORHOOD OF THE N_1 LEVEL. THE DENSITY OF STATES WILL THEN FALL. AT AN ENERGY 0.46 E.V. ABOVE THE N_1 LEVEL, THE SECOND BRILLOUIN ZONE BEGINS WITH THE P-LIKE LEVEL N_1'. THIS IS STILL 3/4 E.V. BELOW THE TOP OF THE FIRST ZONE AT H_{12}, SO THAT THERE IS CONSIDERABLE OVERLAPPING OF THE BANDS. THE TOTAL BAND WIDTH FROM Γ_1 TO H_{12} IS 4.36 E.V., APPROXIMATELY TWO VOLTS LESS THAN WOULD BE EXPECTED ON THE BASIS OF THE EFFECTIVE MASS APPROXIMATION ALONE. THE OCCUPIED PORTION OF THE BAND HAS A WIDTH OF ABOUT 3.1 VOLTS USING E_{Γ_1}, E_2, AND E_4. EQUATION (8) WOULD NOT GIVE A SIGNIFICANTLY DIFFERENT RESULT.

THE STRUCTURE OF THE X-RAY K ABSORPTION EDGE IN POTASSIUM HAS BEEN EXAMINED BY PLATT[28]. DEVIATIONS

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28. J. B. PLATT, PHYS. REV. 69, 377 (1946).

FROM FREE ELECTRON ABSORPTION IN THE DIRECTION OF LESS ABSORPTION ARE NOTICED IN A REGION BEGINNING A LITTLE MORE THAN 1 E.V. ABOVE THE FERMI LEVEL. ONE WOULD EXPECT D STATES TO BE IMPORTANT IN THIS REGION, AND THESE MIGHT SERVE TO REDUCE THE TRANSITION PROBABILITY TO THE 1S CASE LEVEL.

It is interesting to compare the energy bands of potassium with those of the other alkali metals. Since reliable band calculations have not yet been performed for rubidium and cesium, the principal comparison will be with sodium. The band structure of sodium has been studied by many workers, the most recent calculation being those of Ham[11], and Howarth and Jones[29]. Both calculations

29. D. J. Howarth and H. Jones, Proc. Phys. Soc. 65A, 355 (1952).

utilize the cellular method, but Ham's work is based on the Quantum Defect Method and does not utilize an explicit potential.

According to Howarth and Jones the lowest level at the Zone corner H is H_{15}, which is a P like state. Next comes H_{12} and then H_1. (This ordering was also found by Ham.) H_{12} appears to be the lowest state at this point in potassium. At P, the lowest state in sodium is P_1, which is S like. It lies 1.76 ev. below P_4 which mixes P and D states. In potassium, this order is reversed. At N the lowest level according to Howarth and Jones is N_1, but Ham has found N_1', which contains P functions to lie lower than N_1. N_1 appears to be lower in potassium.

It is likely that the principal differences in band forms between sodium and potassium can be explained in terms of increased importance D bands in the latter element. In potassium, the lowest states which contain D functions

TEND CONSISTENTLY TO LIE LOWER THAN STATES CONTAINING ONLY S OR P FUNCTIONS (EXCEPT OF COURSE, FOR THE BASIC 4_s LEVEL Γ_1). THE INCREASED IMPORTANCE OF D LIKE LEVELS SEEMS ALSO TO LEAD TO GREATER DEVIATIONS FROM FREE ELECTRON LIKE BEHAVIOR IN THIS CASE. THAT D STATES SHOULD BE IMPORTANT IN POTASSIUM WOULD NATURALLY BE EXPECTED FROM OBSERVATION OF THE PERIODIC TABLE OF THE ELEMENTS SINCE AS SOON AS THE 4S BAND HAS FILLED IN CALCIUM, THE D BAND BEGINS TO BE OCCUPIED IN SCANDIUM. FOR THIS REASON, ONE WOULD ALSO EXPECT K^4 TERMS IN THE $E(K)$ EXPANSION TO BE MORE IMPORTANT IN POTASSIUM THAN IN LITHIUM OR SODIUM.

VI. HIGHER BANDS

IT IS INTERESTING TO DISCUSS NOT ONLY THE LOWEST BAND BUT ALSO HIGHER LEVELS, IN PARTICULAR P AND D LEVELS TO SEE TO WHAT EXTENT THE BANDS ARE SIMILAR TO THOSE OF OTHER ELEMENTS WHICH HAVE THE BODY CENTERED CUBIC LATTICE. WE WILL BE CONCERNED HERE PRIMARILY WITH THE ORDER OF LEVELS WITHIN A GIVEN BAND, RATHER THAN RELATIVE ORDER OF THE BANDS. WIGNER HAS GIVEN AN INTERESTING ANALYSIS OF THE STRUCTURE OF P AND D BANDS IN THE BODY CENTERED STRUCTURE (30), BASED

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30. E. WIGNER, PROCEEDINGS OF THE INTERNATIONAL CONFERENCE OF THEORETICAL PHYSICS, KISOTO AND TOKYO, SEPTEMBER, 1953, P. 650.

ON POSSIBILITIES OF SATISFYING THE BOUNDARY CONDITIONS WITHIN THE CELLULAR METHOD. HIS WORK IS IN GENERAL AGREEMENT WITH THIS CALCULATION.

WIGNER PREDICTS FOR THE P BAND THAT THE $\underline{K}=0$ STATE Γ_{15} SHOULD BE HIGHEST, THAT THE STATE N_1' SHOULD BE LOWEST WITH A LARGE SEPARATION OF STATES AT THIS POINT, AND THAT THE STATE H_{15} SHOULD BE REASONABLY CLOSE TO THE BOTTOM OF THE BAND. THE CALCULATION CONFIRMS THESE PREDICTIONS. HOWEVER, WIGNER ALSO PREDICTS THAT P_4 SHOULD LIE NEAR THE MIDDLE OF THE BAND WHERE HERE IT HAS BEEN FOUND TO BE CONSIDERABLY LOWER THAN H_{15}. HOWEVER, SOME OF THIS LOWERING MAY BE DUE TO THE D LIKE FUNCTIONS PRESENT IN P_4.

FOR THE D BAND WE FIND N_2 BELOW Γ_{25}' AS PREDICTED. STATES OF $\vec{K}$ PERPENDICULAR TO THE 111 DIRECTIONS; I.E., AT N ARE PREDICTED TO LIE LOWEST. SINCE N_1 MAY BE CONSIDERED TO BELONG TO THE D BAND AS WELL AS TO THE S BAND, THIS STATEMENT IS CORRECT. NOTE THAT H_{12} IS ALSO LOW. WIGNER'S DIAGRAMS OF THE RELATIONS BETWEEN P AND D BANDS ARE INCORRECT IN THIS CASE. ALSO THE STATE P_4 LIES BELOW N_2.

THE GENERAL SHAPE OF THE D BAND FOUND HERE IS IN AGREEMENT WITH A RECENT CALCULATION FOR BODY CENTERED IRON[17] BY THE O.P.W. METHOD, AND IN ALSO WITH THAT FOUND FOR IRON BY A MODIFIED TIGHT BINDING METHOD[31]. WE OBSERVE THAT

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31. F. STERN, PH. D. THESIS, PRINCETON UNIVERSITY, 1955 (UNPUBLISHED).

HERE ALSO, THE SEPARATION OF THE TRIPLY AND DOUBLY DEGENERATE D STATES IS MUCH LESS AT THE CENTER OF THE ZONE THAN AT THE

CORNER H, AND THAT THE MAXIMUM SEPARATION OF THE D BAND IS AT THE POINT N. EXCEPT FOR THE FACT THAT THE O.P.W. IRON CALCULATION HAS N_4 ABOVE N_3, THE RELATIVE ORDER OF THE D LEVELS AT A GIVEN SYMMETRY POINT IS MUCH THE SAME IN IRON AND POTASSIUM. WE NOTE THAT IN ALL THREE CASES, THE TRIPLY DEGENERATE D BAND STATE IS LOWEST AT K=0, BUT THE DOUBLY DEGENERATE STATE IS LOWEST AT H. THE ORDER OF D LEVELS IN POTASSIUM IS ALSO IN AGREEMENT WITH A CALCULATION FOR BODY CENTERED TITANIUM[32], EXCEPT IN THAT CASE,

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32. B. SCHIFF, PROC. PHYS. SOC. 68A, 686 (1955).

A MORE EXTENSIVE CALCULATION WOULD BE DESIRABLE IN ORDER TO MAKE A MORE DETAILED COMPARISON.

THERE IS A SIMPLE DEVICE WHICH SEEMS TO REPRODUCE THE CALCULATED LEVEL ORDER WITHIN A GIVEN BAND VERY WELL IN THIS CASE. LET $\psi_{\underline{K}}^{i}$ REPRESENT THE WAVE FUNCTION FOR THE I TH IRREDUCIBLE REPRESENTATION OF THE WAVE VECTOR $\underline{K}$. $\psi_{\underline{K}}^{i}$ IS EXPANDED IN ORTHOGONALIZED PLANE WAVES:

$$\psi_{\underline{K}}^{i} = \Sigma_{\underline{H}} \beta_{\underline{K},\underline{H}}^{i} X_{\underline{K}+\underline{H}} \qquad (9)$$

WHERE $X_{\underline{K}+\underline{H}}$ IS GIVEN BY (3). THE VECTOR $\underline{H}$ RUNS OVER ALL RECIPROCAL LATTICE VECTORS. THE LEVELS MAY BE ORDERED ACCORDING TO THE QUANTITY $(\underline{K}+\underline{H}')^2$ WHERE $(\underline{K}+\underline{H}')$ IS THE O.P.W. OF LOWEST ENERGY BELONGING TO $\psi_{\underline{K}}^{i}$. SINCE THIS IS AN ORDERING ACCORDING TO KINETIC ENERGY, THERE IS A ROUGH RESEMBLANCE TO THE PRINCIPLE OF MAXIMUM SMOOTHNESS[31].

THIS PROCEDURE SAYS IN ESSENCE, THAT THE ORDER OF LEVELS IN A GIVEN BAND IS WHAT WOULD BE EXPECTED FOR FREE ELECTRON BANDS. IT IS NOT SURPRISING THAT IT GIVES THE CORRECT RESULTS FOR POTASSIUM. IT IS MORE INTERESTING THAT IT SEEMS TO WORK REASONABLY WELL IN IRON. EVEN IN POTASSIUM, HOWEVER, ONE MUST NOT SUPPOSE THAT THE NUMERICAL ENERGY VALUES OF THE LEVELS WILL BE IN GOOD AGREEMENT WITH A FREE ELECTRON MODEL. INSPECTION OF FIGURE 2 WILL REVEAL THAT SOME LEVELS WILL CONNECT BY BANDS WHICH MUST DEPART SEVERELY FROM THE FREE ELECTRON FORM.

THE SUCCESSFUL COMPARISON OF THESE RESULTS WITH OTHER CALCULATIONS FOR THE VARIOUS BANDS SUGGESTS THAT AT LEAST THE RELATIVE ORDER OF LEVELS WITHIN A GIVEN BAND IS NOT VERY SENSITIVE TO DETAILS OF THE POTENTIAL. IT IS POSSIBLE, THEN, THAT THE GENERAL FORMS OF INDIVIDUAL S, P AND D BANDS ARE NOW WELL UNDERSTOOD FOR THE BODY CENTERED CUBIC LATTICE. IT IS IMPORTANT TO NOTE, HOWEVER, THAT THE SITUATION IN REGARD TO OVERLAP OF THESE BANDS IS MUCH LESS CLEAR BECAUSE THE OVERLAP IS MUCH MORE SENSITIVE TO THE POTENTIAL[17]. IT IS INTERESTING TO NOTE THAT THERE IS APPARENTLY A VERY CONSIDERABLE DEGREE OF OVERLAP IN POTASSIUM.

SINCE THERE IS EVIDENCE THAT THE GENERAL FORM OF A BAND IS REASONABLY INDEPENDENT OF POTENTIAL IT IS INTERESTING TO CONSIDER THE FORM OF THE F BAND. AT K=0, THE STATES Γ_{25},

Γ_2', AND Γ_{15} CONTAIN F FUNCTIONS. AT P WE HAVE P_4, P_5, AND P_1, AND AT N WE HAVE N_2', N_1', N_4', N_3'. THE LOWEST PREDOMINANTLY F LIKE STATE IS Γ_{25}, AND THE TOP OF THE BAND ALSO APPEARS TO OCCUR AT Γ WITH Γ_2'. THIS ORDER IS REVERSED WITH: H_2' LIES BELOW H_{25}. WE FIND Γ_{15} INTERMEDIATE BETWEEN Γ_{25} AND Γ_2' AND H_{15} INTERMEDIATE BETWEEN H_2' AND H_{25}. AT P, THE ORDER IS APPARENTLY P_5, P_4, AND P_1. AT N, N_1' IS APPARENTLY THE LOWEST FOLLOWED BY N_4', N_2', N_3', N_1', N_4', AND N_3' IN THAT ORDER. WE CONSIDER HERE THE SECOND AND THIRD LEVELS OF THIS CLASS TO BE F LIKE. (NOT ALL OF THE ENERGIES OF THE LATTER STATES ARE GIVEN IN TABLE III.)

I AM INDEBTED TO MR. J. SEGAL, MR. E. L. HAASE, AND MR. D. E. JACK FOR ASSISTANCE WITH THE RATHER LABORIOUS COMPUTATIONS. THE ASSISTANCE OF PROFESSOR R. D. WOODS AND MR. S. BERMAN IN THE EARLY STAGES OF THIS CALCULATION IS GRATEFULLY ACKNOWLEDGED.

TABLE I

THE QUANTITY RV IS GIVEN IN ATOMIC UNITS FOR S, P, AND D STATES, AND FOR THE COULOMB POTENTIAL.

R	RV_S	RV_P	RV_D	RV_C
.00	38.00	38.00	38.00	38.00
.01	36.78	36.76	36.70	36.52
.02	35.61	35.57	35.49	35.12
.03	34.51	34.39	34.30	33.82
.04	33.46	33.30	33.19	32.63
.05	32.53	32.27	32.15	31.54
.06	31.64	31.32	31.19	30.54
.07	30.83	30.41	30.29	29.61
.08	30.12	29.58	29.46	28.75
.09	29.60	28.77	28.67	27.93
.10	28.42	28.02	27.93	27.15
.15	24.78	24.77	24.70	23.74
.20	22.22	22.12	21.92	20.86
.25	20.10	20.00	19.62	18.50
.30	18.33	18.29	17.67	16.57
.35	16.99	16.82	16.00	15.02
.40	16.08	15.64	14.64	13.76
.50	13.41	13.73	12.56	11.81
.60	10.91	12.08	11.06	10.29
.70	9.86	10.48	9.87	8.98
.80	8.85	8.84	8.88	7.83
.90	7.93	7.94	8.02	6.81
1.00	7.15	7.17	7.26	5.93
1.10	6.47	6.50	6.56	5.17
1.20	5.93	5.95	5.94	4.54
1.40	5.321	5.093	4.887	3.598
1.60	4.262	4.526	4.054	2.982
1.80	3.090	3.462	3.428	2.595
2.00	2.545	2.839	2.971	2.357
2.50	2.286	2.199	2.350	2.099
3.00	2.130	2.049	2.141	2.025
3.50	2.055	2.020	2.076	2.006
4.00	2.025	2.009	2.035	2.001
4.50	2.009	2.005	2.013	2.000

TABLE II

FOURIER COEFFICIENTS OF POTENTIAL ARE GIVEN IN RYDBERGS AS FUNCTIONS OF THE NUMBER $M^2 = (\frac{A}{2\pi} \underline{K})^2$. ONLY EVEN INTEGRAL VALUES OF M^2 OCCUR FOR THE BODY CENTERED CUBIC STRUCTURE.

M^2	$V_S(M)$	$V_P(M)$	$V_D(M)$	$V_C(M)$
0	.8677	.8692	.8748	.7924
2	.2841	.2900	.2843	.2346
4	.2314	.2369	.2281	.1965
6	.1865	.1913	.1824	.1612
8	.1489	.1525	.1439	.1298
10	.1249	.1266	.1192	.1106
12	.1143	.1143	.1097	.1035
14	.1000	.0996	.0973	.0922
16	.0879	.0875	.0864	.0821
18	.0775	.0772	.0769	.0733
20	.0686	.0685	.0688	.0657
22	.0631	.0632	.0636	.0610
24	.0585	.0596	.0594	.0572
26	.0540	.0552	.0562	.0558

TABLE III

LOWEST ENERGY STATES IN POTASSIUM (ENERGIES IN RYDBERGS).

REPRESENTATION	ORDER OF DETERMINANT	NO. OF WAVES	ENERGIES		
		S-LIKE STATES			
Γ_1	8	135	-.4304	+.8346	
H_1	4	62	+.2651	+.9760	
P_1	4	40	+.0544	+1.1415	
N_1	5	22	-.2239	+.2682	+.6274
		P-LIKE STATES			
Γ_{15}	4	42	+.6986	1.3277	
H_{15}	4	38	+.0621	+.9057	
P_4	4	18	-.1262	+.9340	
N_1'	4	18	-.1902	+.5561	
N_3'	4	20	-.1765	.7813	
N_4'	4	20	+.3561	1.0721	
		D-LIKE STATES			
Γ_{25}'	4	18	+.2200	+1.4814	
Γ_{12}	4	54	+.2640	+.9263	
H_{25}'	4	56	+.5372	+1.2726	
H_{12}	4	54	-.1322	+1.1224	
P_3	3	36	+.4856	+1.3603	
N_2	4	24	+.0552	+.8447	
N_3	4	28	+.6939	+1.2785	
N_4	4	24	+.4363	.8300	
		F-LIKE STATES			
Γ_{25}	3	48	+.2897	+1.8382	
Γ_2'	2	32	+1.7401	4.1990	
H_{25}	3	48	1.4246	1.5285	
H_2'	3	56	+.7046	+2.8097	
P_5	3	36	+.5967	+1.3760	
N_2'	3	24	+.8945	2.0873	

TABLE IV

LOWEST EIGENVALUE BY ORDER FOR Γ_1 (IN RYDBERGS). THE T LOWEST SIX EIGHTH ORDER EIGENVALUES ARE ALSO GIVEN.

ORDER	LOWEST $E\Gamma_1$
1	-.2371
2	-.3834
3	-.3900
4	-.4049
5	-.4125
6	-.4232
7	-.4246
8	-.4304

LOWEST 6 EIGENVALUES IN EIGHTH ORDER

-.4304

+.8346

1.1476

1.2621

1.3309

1.4525

CAPTIONS FOR FIGURES

FIGURE 1.

BRILLOUIN ZONE FOR THE BODY CENTERED CUBIC LATTICE.

FIGURE 2.

ORDER OF THE ENERGY LEVELS AT THE FOUR SYMMETRY POINTS Γ, H, P, AND N. ALL LEVELS WITH $E < 1$ RY. ARE SHOWN.

FIGURE 3.

LOWEST ENERGY BAND ALONG 100 AXIS IN THE BRILLOUIN ZONE AS GIVEN BY EQUATION (8) (SOLID LINE), AND AS GIVEN BY A FREE ELECTRON APPROXIMATION FOR $M/M^* = 1.168$ (BROKEN LINE).

FIGURE 4.

LOWEST ENERGY BAND ALONG 110 AXIS IN THE BRILLOUIN ZONE AS GIVEN BY EQUATION (8) (SOLID LINE), AND AS GIVEN BY A FREE ELECTRON APPROXIMATION FOR $M/M^* = 1.168$ (BROKEN LINE).

FIGURE 5.

DENSITY OF STATES IN ARBITRARY UNITS AS A FUNCTION OF ENERGY.

FIG #1

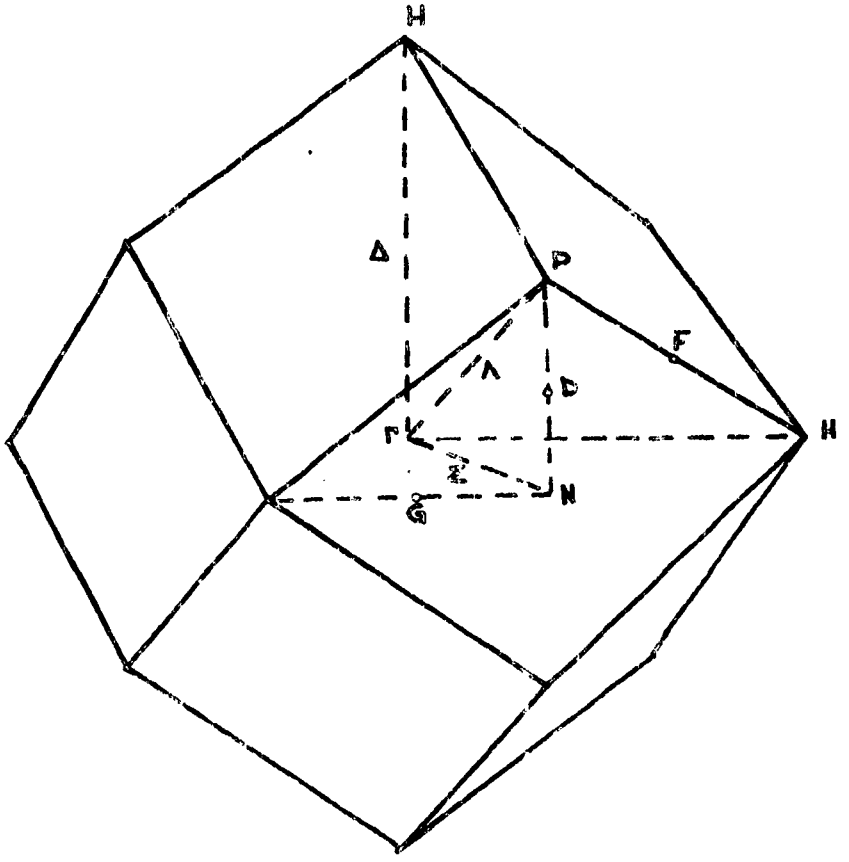

FIG #2

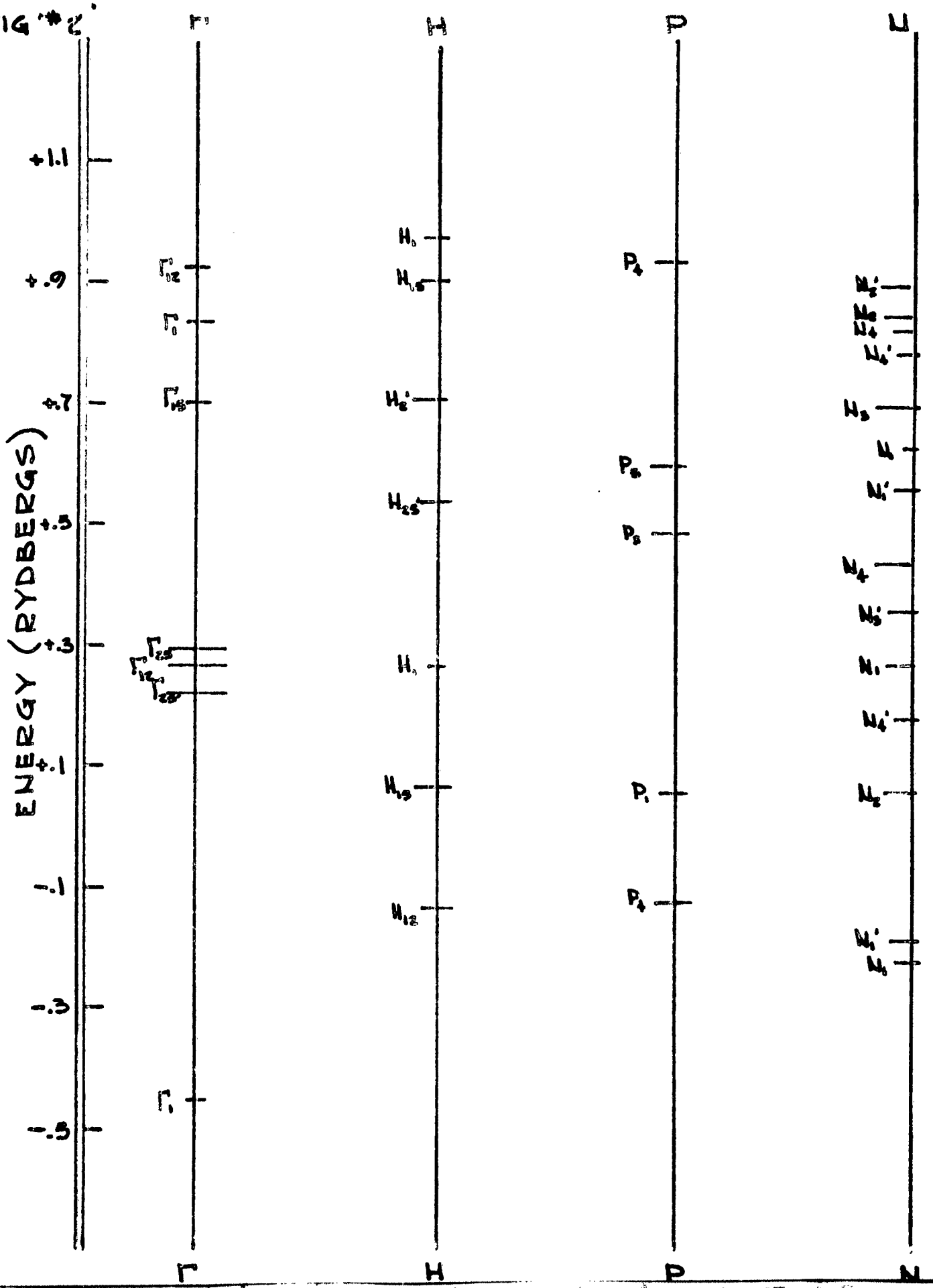
ENERGY (RYDBERGS)
+1.1
+.9
+.7
+.5
+.3
+.1
-.1
-.3
-.5
Γ
H
P
N
Γ12
Γ1
Γ15
Γ25
Γ12
Γ25'
Γ1
H0
H15
H2'
H25'
H1
H12
H12
P4
P5
P3
P1
P4
N2'
N3
N4
N4'
N3
N1
N1'
N4
N5'
N1
N4'
N2
N1'
N1

FIG #3

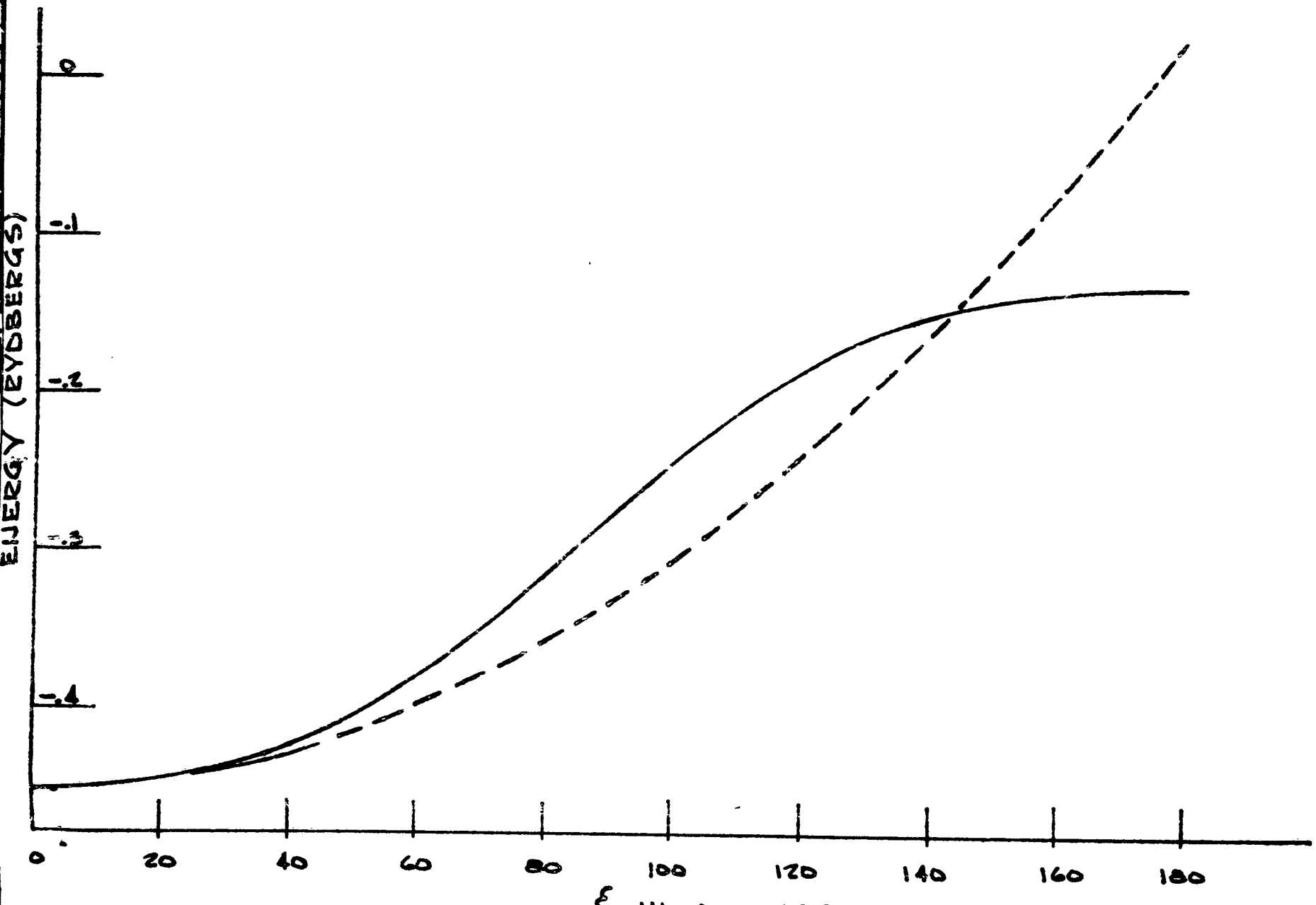

FIG #4

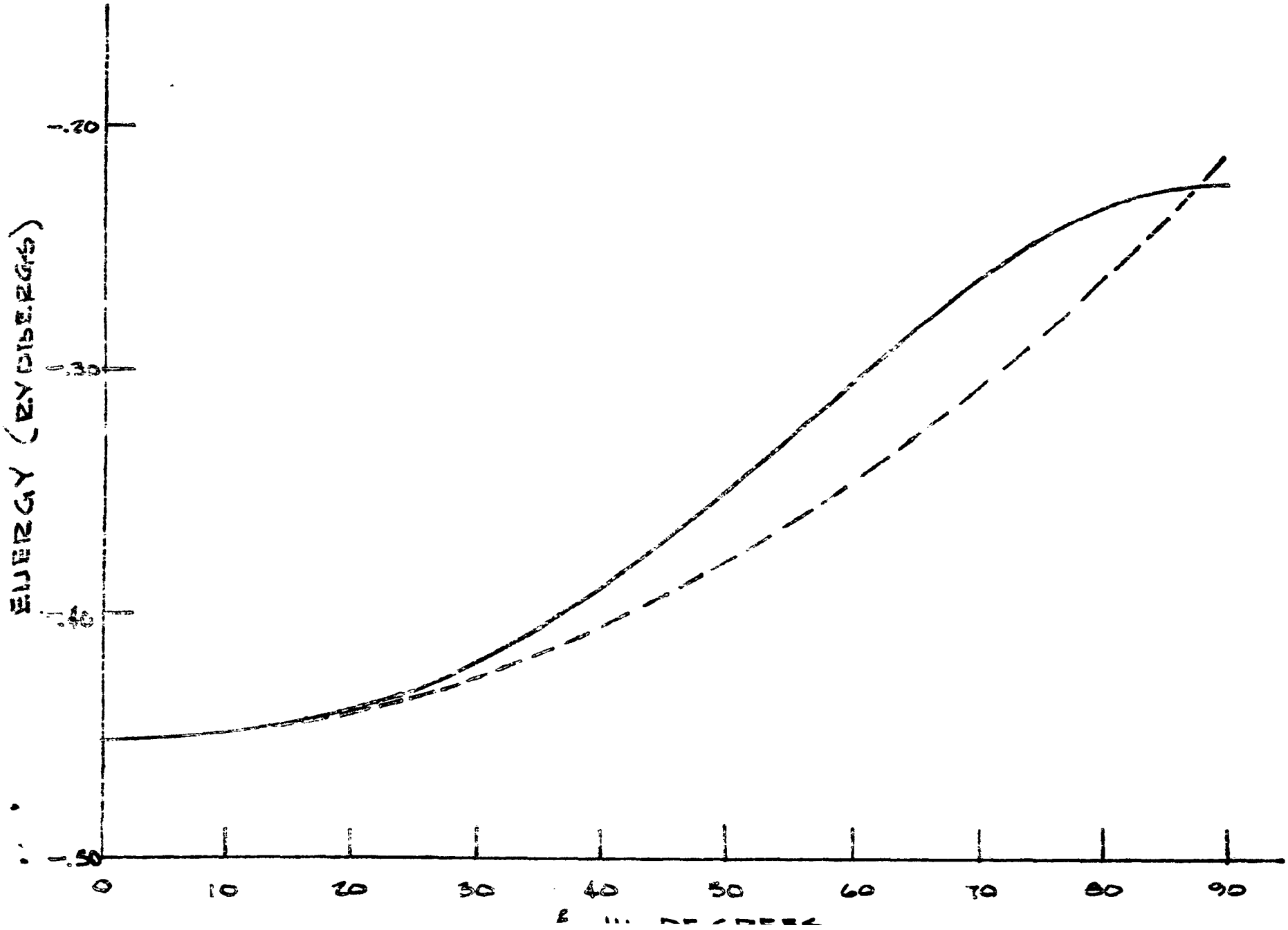
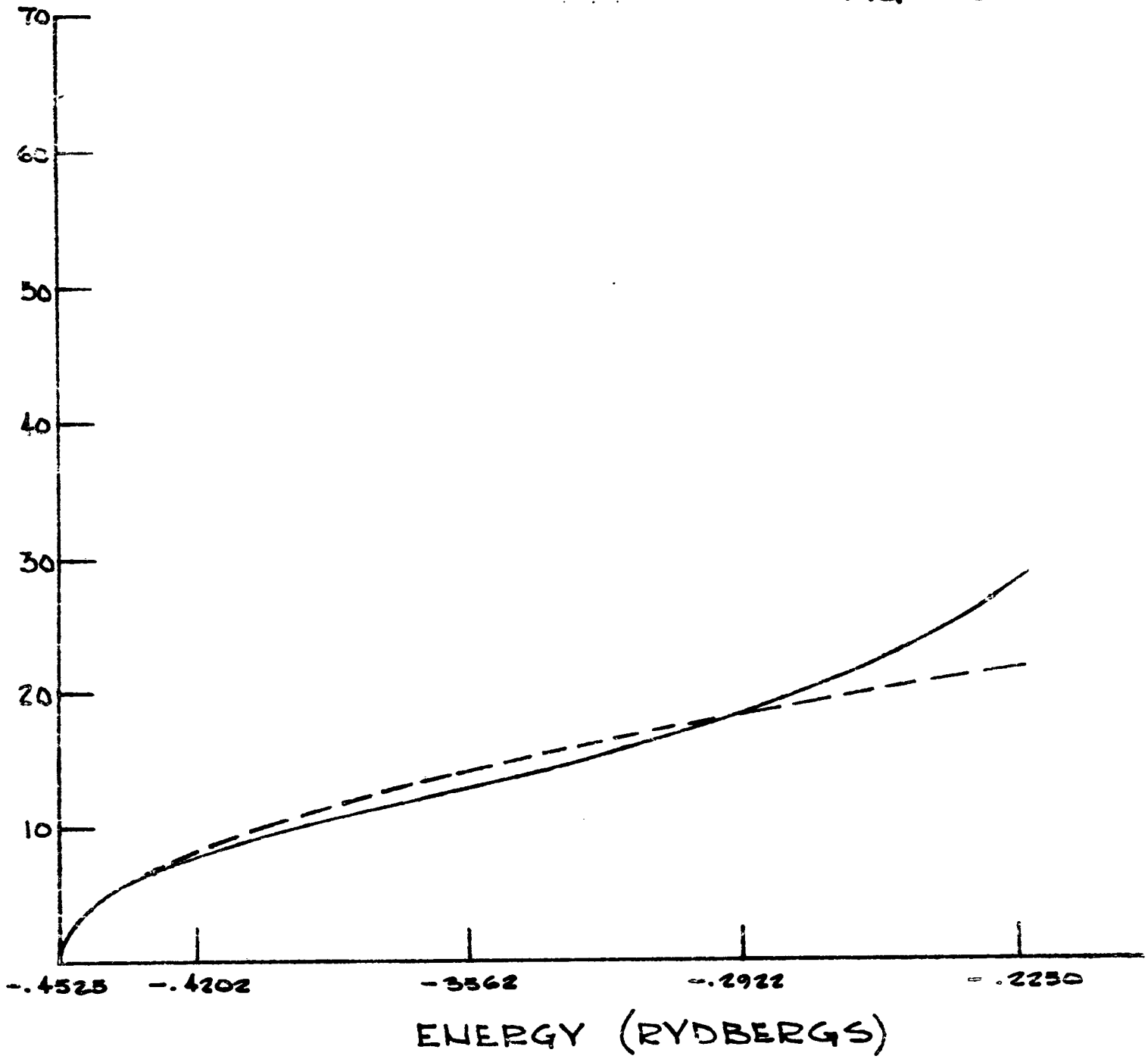
FIG #5