Electron Momentum Distribution in Silicon and Germanium by Positron Annihilation*

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The angular correlation of positron-annihilation radiation from single crystals of silicon and germanium has been measured for three different orientations of each crystal. The distributions for the three orientations differ greatly from one another, but each germanium distribution differs from the corresponding silicon distribution only by a scale factor which arises from the difference in the lattice constant. Data are compared with curves calculated using the nearly free-electron approximation for the electron's momentum. It is assumed that the occupied electron states in the crystal fill the Jones zone, a regular dodecahedron bounded by the set of {220} planes in momentum space, and the energy gap is taken to be an adjustable parameter. The fit is extremely good for the radiation emitted in the (110) plane but not so good for the (111) and (100) orientations. Possible reasons for the discrepancies are discussed.

INTRODUCTION

SINCE the work of Berko, Kelley, and Plaskett[1] on positron annihilation in oriented graphite, numerous workers have observed anisotropies in the momentum distributions of annihilation radiation from oriented single crystals.[2–4] Most of this work has been done on metals, where it was hoped that positron annihilation could provide another tool for studying the Fermi surface. It has been shown[5] that a positron in a metal reaches thermal energy in a time short compared with its mean lifetime; therefore, the main contribution to the momentum of an annihilation pair comes from the electron, and this momentum is observed by measuring the angle between the two annihilation gamma rays. However, one does not obtain the conduction-electron momentum distribution directly by this measurement, for the situation is complicated by the departure of the electron and positron wave functions from plane waves, by annihilation with core electrons, and possibly by electron-positron interactions.

In order to clarify the problem, it seemed worthwhile to study materials in which the momentum distribution of the valence electrons is presumably well known. A successful study of a semiconductor would not only verify the correctness of our thinking, it would demonstrate the power of the positron-annihilation technique, for the over-all momentum distribution of a semiconductor is inaccessible to the usual type of Fermi-surface measurement. This paper reports a study of the angular distribution of annihilation radiation from three different orientations of single crystals of silicon and germanium.

EXPERIMENTAL

The physical arrangement of the experimental apparatus is shown in Fig. 1. A parallel-slit arrangement is used with counter slits 12-in. high and 1-mm wide. The slits are placed 2.1 m from the sample. NaI(Tl) crystals 12-in. long and 2 in. in diameter are used to detect the annihilation radiation. The slits are placed on the pivot ends of 2.1-m-long arms whose other ends are linked together beneath the sample. To change the angle of investigation the sample and source together are moved at right angles to the plane defined by the two counter slits. The two counter slits, resting on the ends of the arms, turn so as to subtend the same solid angle at the sample. The positioning mechanism is automated so that counts are recorded for fixed times (15 min) at a set of predetermined angles. The counts are accumulated in a printing register and printed out at the end of each counting interval.

The samples were of various sizes. The silicon (100) and (110) samples were plates 1.5 by 5 by 0.1 cm thick. The rest [(111) silicon and (100), (110), and (111) germanium] were about 2 by 0.7 by 0.1 cm thick. All were mounted with the long dimension, parallel to the counter slits, and the 0.1-cm edge facing the counters. Back-reflection Laue photographs of these crystals show that the crystallographic axes are within 3 deg of the

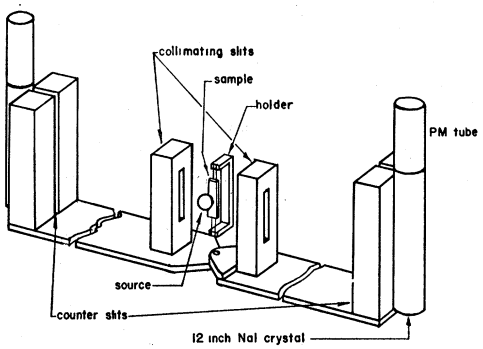

FIG. 1. Experimental arrangement.

* This work supported in part by the U. S. Atomic Energy Commission.

[1] S. Berko, R. E. Kelley, and J. S. Plaskett, Phys. Rev. **106**, 824 (1957).

[2] S. Berko and J. S. Plaskett, Phys. Rev. **112**, 1877 (1958).

[3] S. Berko, Phys. Rev. **128**, 2166 (1962).

[4] A. T. Stewart, J. B. Shand, J. J. Donaghy, and J. H. Kusmiss, Phys. Rev. **128**, 118 (1962).

[5] G. E. Lee-Whiting, Phys. Rev. **97**, 1557 (1958).

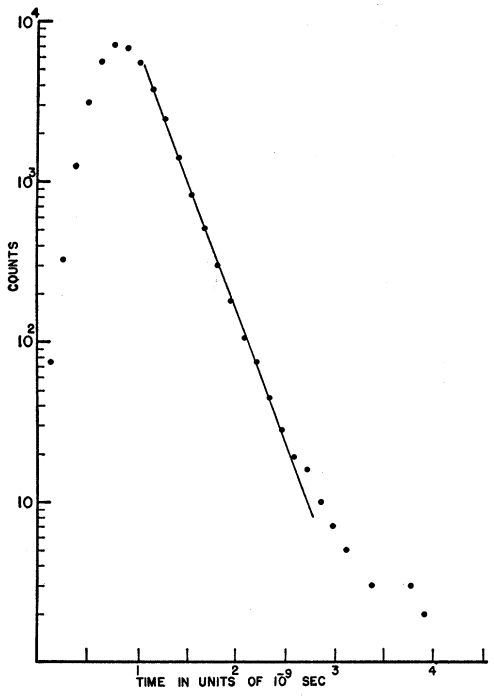

FIG. 2. Time distribution of positron annihilations in silicon.

normal to the large face of the crystals. Prior to mounting, the samples were lightly lapped, etched with CP-4, and thoroughly rinsed in distilled water. Care was taken to avoid contamination of the sample faces presented to the positron source (5 mCi of Na^{22}).

The samples were mounted by cementing them with cellulose glue to 1-mil tungsten wires stretched across the mouth of a U-shaped sample holder. The collimating slits were so designed that the counter slits could see only the sample and some of the support wires. The number of annihilations in the support wires is negligible compared with those in the sample. The samples were turned slightly about the vertical axis so that one counter sees only the sample face while the other sees only the back. This makes the absorption of gamma rays by the sample relatively constant. The effective width of the sample face as seen by the counter is no more than 0.05 cm. This causes an effective broadening of the instrumental resolution function by about $\frac{1}{2}$ mrad.

All data presented here were taken with the samples surrounded with a helium atmosphere. Small asymmetries noted in early data were traced to annihilations of positrons with electrons in the air in front of the sample. The long mean free path of positrons in helium renders this effect negligible.

A conventional fast-slow coincidence circuit is used in conjunction with two Hamner N-302 amplifier-pulse height selectors to detect the annihilations. The output of the fast-slow coincidence circuit drives a printing register via a tunnel-diode resolver.[6] When the counting rate is high the resolver prevents the loss of counts due to the dead time of the mechanical register.

A measurement was made of the lifetime distribution of the positrons in silicon. This measurement used a time-to-amplitude converter of the type described by Bell[7]; the resolution (full width at half-maximum of the curve produced by Co^{60} gamma rays) was 0.6 nsec. The over-all arrangement was that described by McGervey and Walters.[8]

RESULTS

Figure 2 shows the time distribution of annihilations of positrons in silicon. The lifetime curve is a single exponential with decay constant of 0.26 nsec. The presence of a single exponential with a short lifetime gave confidence that the positrons are annihilating as free positrons rather than from some sort of bound state. Presumably positrons behave similarly in germanium.

The angular distributions obtained for the three orientations of silicon and germanium are shown in Figs. 3 and 4. Distributions obtained for the same orientation in silicon and germanium are quite similar, the silicon distribution being slightly wider. These curves represent the superposition of two or more separate runs for each orientation. A minimum of 10 000 counts were accumulated in the peak for each run.

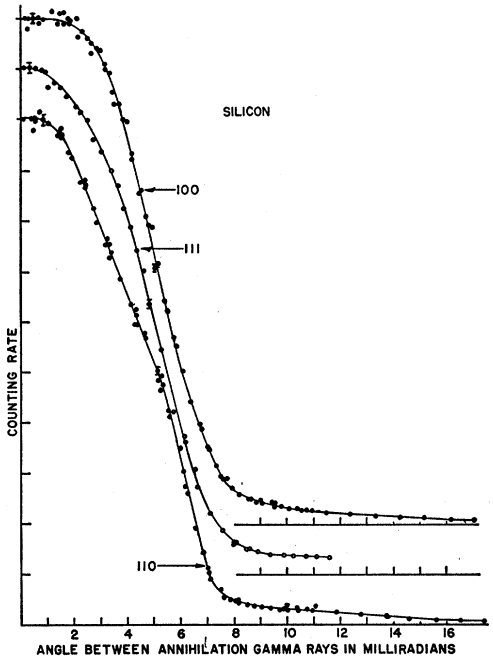

FIG. 3. Experimental angular distributions from Si oriented along the [111], [110], and [100] directions.

[6] J. D. McGervey, Nucl. Instr. Methods 14, 351 (1961).

[7] R. E. Bell, *Alpha- Beta- and Gamma-Ray Spectroscopy*, edited by K. Siegbahn (North-Holland Publishing Company, Amsterdam, 1965), p. 922.

[8] J. D. McGervey and V. F. Walters, Nucl. Instr. Methods 25, 219 (1964).

Notice the rather sharp downward break in the curve for the [110] orientation at about 6 mrad.

The over-all shape of the curve for the [111] orientation agrees with that reported by Columbino, Fiscella, and Trossi.[9] However, we do not observe the small secondary peaks which they reported at about 10 mrad. Collection of an additional several thousand counts at each point in the vicinity of 10 mrad for germanium failed to reveal any such structure; it is clear from other details of the curves that our angular resolution should have been sufficient to reveal such structure.

ANALYSIS

The tail components at large momentum values are small for both silicon and germanium, implying that the character of the distributions is determined primarily by the valence-electron structure. Since the core electrons have large momenta, in general, annihilations with core electrons would cause a much larger tail distribution.

Columbino *et al.*[9] explained their distributions for the [111] orientations of silicon and germanium single crystals by considering the momentum distributions of the orbitals of the free atom. We have examined this approach and found that it is unable to explain the observed differences among the three orientations, predicts a much larger tail than is observed experimentally, and is unable to explain the increase in slope for the [110] orientation.

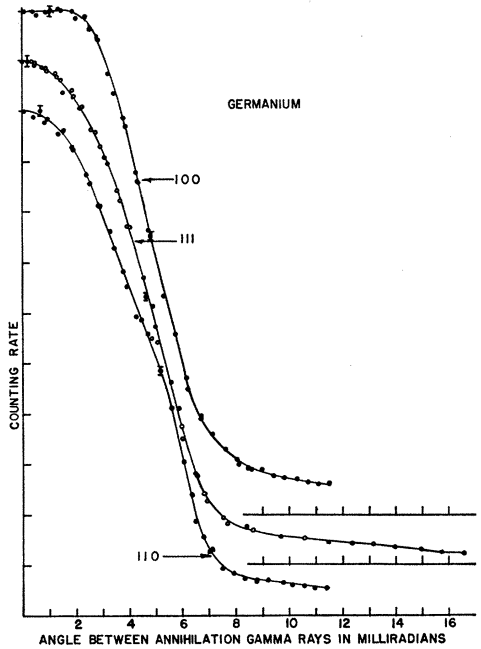

FIG. 4. Experimental angular distributions from Ge oriented along the [111], [110], and [100] directions.

[9] P. Columbino, B. Fiscella, and L. Trossi, Nuovo Cimento 31, 950 (1964).

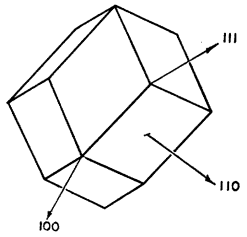

FIG. 5. The Jones zone for silicon and germanium (diamond structure).

One might expect to find a better approach by referring to the many band-structure calculations in the literature.[10,11] Unfortunately the information needed for the analysis of our data is not obtainable from these papers. To analyze our data, one needs to know the amplitudes of all the Fourier components of all the occupied valence-electron states. In a band-structure calculation an enormous number of Fourier components are often used, but this is done only for those wave functions which have certain symmetry properties. It did not seem feasible to us to attempt a band-structure calculation on the scale necessary for analysis of our data.

Many features of our results can be understood by reference to a simple free-electron model. It may seem excessively crude to use such an approach for a semiconductor, but Harrison[12] has achieved some success with similar calculations on silicon.

When using a free-electron model it is convenient to work with the extended-zone scheme. In this picture the semiconducting properties may be accounted for by assuming that the occupied states just fill a geometric figure bounded by Bragg reflection planes in momentum space. The energy gap across these planes makes it energetically favorable for the states inside the zone to be filled, rather than states outside the zone.

Mott and Jones[13] have investigated this problem and have pointed out that the energy gap is zero across those planes for which the x-ray structure factor vanishes. Such planes presumably could not form part of the bounding surface of the extended-zone figure and still retain the semiconducting properties of the material.

For the diamond structure of silicon and germanium, the structure factor is particularly large for the set of {220} planes. The volume bounded by these planes holds just four electrons per atom, so if the energy gap were large enough this volume could still contain all of the occupied states, thereby accounting for the semiconducting properties of silicon and germanium. The regular dodecahedron formed by the set of {220} planes is

[10] J. Callaway, *Energy Band Theory* (Academic Press Inc., New York, 1964), pp. 157–173.

[11] F. Herman, Rev. Mod. Phys. 30, 102 (1958).

[12] W. A. Harrison, General Electric Research Laboratory, Schenectady, New York, 1964, Report No. 64-RL-(3712M) (unpublished).

[13] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, England, 1936), pp. 152–159.

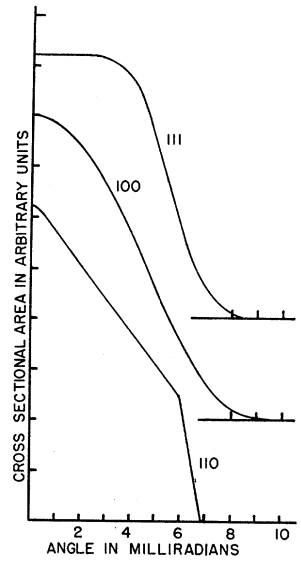

FIG. 6. Area of cross sections through the Jones zone perpendicular to the [111], [110], and [100] directions. A 1-mrad-square resolution function has been folded into each curve.

known as the large or Jones zone (Fig. 5). If the electrons were unperturbed plane waves, then the parallel-slit apparatus, being sensitive to annihilations with a particular component of momentum p_z, would yield a distribution which is proportional to the cross-sectional area of slices through the Jones zone.

Figure 6 shows cross-sectional areas of the Jones zone perpendicular to the [100], [111], and [110] directions, respectively, with the experimental resolution folded in. The curves for the [100] and [111] directions do not greatly resemble the experimental curves, but the curve for the [110] direction fits the experimental curve extraordinarily well. It is hard to believe that such a fit could be purely accidental.

One should not, of course, expect the simple cross-sectional areas of the Jones zone to fit well for all three directions, for the very fact that an energy gap exists indicates that the electron wave functions are perturbed and they contain higher Fourier components. However, the fit for all three directions is close enough to suggest that one should go one step further with the nearly free-electron model, by using it to calculate, by the method described by Mott and Jones,[14] the Fourier components introduced by interaction with the {220} planes.

Berko and Plaskett[2] have used this method in their analysis of their data on copper. They show from the nearly free electron theory that the momentum distribution of the photon pair produced on annihilation, assuming the positron wave function to be constant, is

$$|A(\mathbf{k})|_{\pm}^2=\tfrac{1}{2}[1\mp x(1+x^2)^{-1/2}], \qquad (1)$$

where

$$x=\boldsymbol{\alpha}\cdot(\tfrac{1}{2}\boldsymbol{\alpha}-\mathbf{k})/Eg.$$

Eg is the band gap energy, $\boldsymbol{\alpha}$ a reciprocal lattice vector of the crystal, and $\mathbf{k}$ the wave vector of the electron wave. The upper and lower signs refer to the upper and lower bands. The assumption of a constant positron wave function appears from the data to be an acceptable one. Any appreciable curvature in the positron wave function would produce higher Fourier components which could be seen in the tail of the observed distribution.

If the probability of annihilation with a given electron is independent of its momentum,[15] then the probability that the two photons carry off momentum component

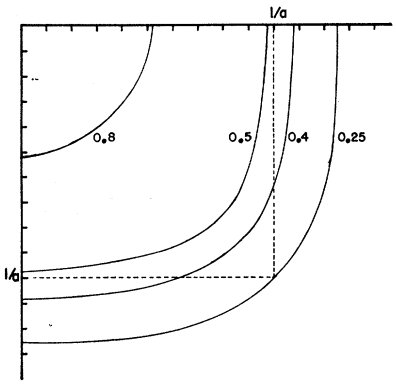

FIG. 7. Contours of constant $|A(k)|^2$ for a two-dimensional square zone with arbitrary energy gap. The 0.5 contour asymptotically approaches each zone boundary.

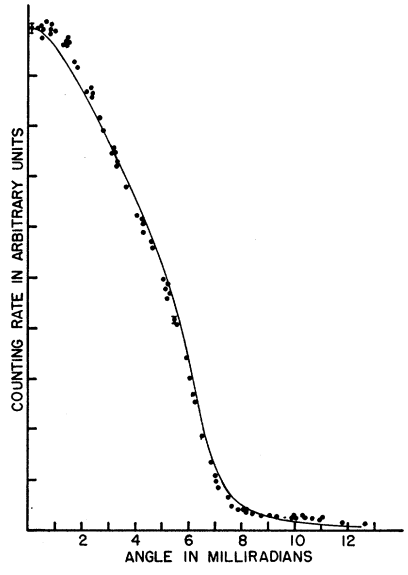

FIG. 8. Angular distribution for Si [110] orientation. The points are the experimental data with a portion of the tail subtracted (see text). The solid curve is the distribution predicted from the Jones zone model. Curves are normalized to equal areas.

[14] Reference 13, pp. 59–63.

[15] This assumption is open to question. Kahana [Phys. Rev. **129**, 1622 (1963)] has explained positron mean lives by an "enhancement factor" which introduces a momentum dependence into the annihilation rate. We neglect this factor in our analysis, for it is not clear how it should be applied to a semiconductor, particularly at a zone boundary.

p_z is

$$N(p_z)=\int\int |A(\mathbf{k})|^2 dk_x dk_y. \quad (2)$$

When one considers more than one zone boundary,

$$|A(\mathbf{k})|^2=\prod_{i=1}^{n}|A_i(\mathbf{k})|^2, \quad (3)$$

where $A_i(\mathbf{k})$ is the amplitude resulting from interaction with the ith zone boundary, and there are n zone boundaries to be considered. Figure 7 shows $|A(\mathbf{k})|^2$ for a two-dimensional filled zone with no overlap into the next zone.

In evaluating Eq. (3) only those faces which are not parallel to p_z are considered. The parallel faces do introduce higher Fourier components into the wave function but in the first approximation they have the same component of p_z as the unperturbed state and so cannot be distinguished from it. We have neglected the interaction of these higher Fourier components with the zone boundaries. When this integral was evaluated for the various orientations of the Jones zone, 10, 8, and 6 zone boundaries were considered for the z axis parallel to the directions [110], [100], and [111], respectively. The region outside the Jones zone boundaries was assumed to be made up entirely of right prisms with rhombic bases. The bases of these prisms are the faces of the Jones zone. The wedge-shaped regions between the prisms were neglected.

For each orientation a curve was calculated for each of several values of the energy gap, with the energy gap assumed to be constant over the entire zone face. Each curve was constructed from values of the integral in (2) for thirty different values of p_z. The integral was evaluated numerically on the Univac 1107 digital computer at the Case Institute of Technology Computing Center. In order to compare these curves directly with experiment we have folded the instrumental resolution function into the theoretical curve, using a 1-mrad-square resolution as a reasonable approximation to the actual instrumental resolution. The resulting theoretical curves are shown superimposed on the experimental distributions in Figs. 8, 9, and 10. These experimental distributions have the background and a portion of the tail subtracted from them. The amount subtracted was determined by assuming that the valence-electron distribution goes to zero where the theoretical distribution goes to zero. The amount of tail at this point was assumed to be constant from that point on in to $p_z=0$. Thus we have assumed that the valence distribution sits on a pedestal above the base line. Admittedly this is a very rough approximation to the true shape of the tail; however, the tail is small and is thought to be slowly varying so that the exact form of our tail approximation is not overwhelmingly important.

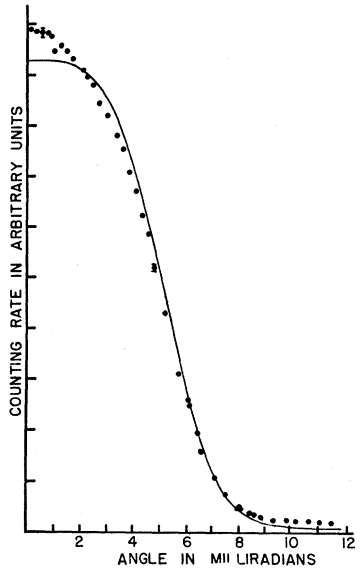

FIG. 9. Angular distribution for Si [111] orientation. Data and theory presented as in Fig. 7.

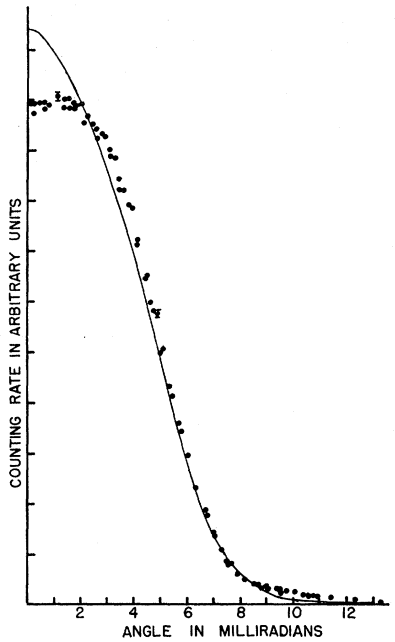

FIG. 10. Angular distribution for Si [100] orientation. Data and theory presented as in Fig. 7.

CONCLUSIONS

The simple Jones zone model agrees extremely well with the data for the [110] orientation. In particular the downward break of the curve near 6 mrad is well explained. In this orientation the slices through the zone are parallel to one face so that the distribution falls off rapidly in the vicinity of this face.

For the [111] and [100] orientations the model produces curves of the correct width, but their shape does not agree so well with experiment, especially near the center. This is not too surprising, in view of the many approximations made in the calculation. Perhaps the most serious of these is that we have ignored the pres-

ence of the {111} and {311} planes, which have nonzero structure factor and may therefore be expected to affect the momentum distribution, especially in the regions where they are close to the {220} planes. The effect of these planes may show up more strongly in the [111] and [100] orientations; because in these orientations the {220} planes are inclined with respect to p_z so that no one plane plays a dominant role at any point in the distribution.

Each calculated curve in Figs. 8, 9, and 10 was obtained by assuming an energy gap of 5 eV. The energy gap in our calculation is the discontinuity in energy corresponding to a direct transition; this is much larger than the energy difference between the highest valence-band level and lowest conduction-band level. Reflectance experiments[16] yield values of the energy gaps on the order of 3–4 eV for direct transitions. Comparison of Fig. 6 (zero energy gap) with Fig. 10 shows that the fit would not be changed greatly by use of a gap of 3–4 eV rather than 5 eV.

[16] H. Ehrenreich, H. R. Phillip, and J. C. Phillips, Phys. Rev. Letters 8, 59 (1962).

SUMMARY

We have observed marked anisotropies in the angular distribution of annihilation from silicon and germanium single crystals. The simple Jones-zone model predicts distributions which are similar enough to the actual ones, particularly in the widths, to give confidence that this picture has some relevance. It is possible that better agreement could be obtained by a similar calculation which included the effects of the {311} and {111} planes, but such a calculation would be very tedious. It is also possible that the lack of agreement is an indication that the nearly free-electron model cannot be pushed this far.

ACKNOWLEDGMENTS

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Electronic Band Structure in the Sodium Iodide Crystal*†

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The electronic band structure of sodium iodide has been calculated by using the tight-binding method for the valence bands and an empirical method for the lowest conduction bands. Functions for the I^- and Na^+ ions have been obtained by solving the Hartree-Fock-Slater modified equation. The $5p$ and $5s$ I^- functions are allowed to mix at appropriate points in the Brillouin zone. The lattice parameter is varied and yields results for shifts in energy which agree with those observed when the lattice temperature is changed. Spin-orbit interactions are included and yield results for the $5p$ bands which are in agreement with experiment. Effective masses for electrons and holes are calculated at the points Γ, L, and X in the valence and conduction bands.

I. INTRODUCTION

THE band structure of the alkali halides has been considered in various degrees of detail and success by use of the tight-binding method. This method also seems to be useful for calculations on other ionic crystals and the rare gases. In the present work, the structure of NaI is considered. Previously, most of the work has been on the alkali chlorides. Casella[1] investigated the structure of NaCl, Howland[2] investigated KCl, and Kunz and Van Sciver[3] investigated LiCl. Calculations of interest other than those for alkali halides are for solid krypton by Fowler[4] and AgCl by Bassani, Knox, and Fowler.[5] The result of Casella, Howland, and Bassani, Knox, and Fowler ignore spin-orbit interaction insofar as giving band structures with spin-orbit interactions included. In presenting his results, Casella did not consider the possibility of mixing of other states with the $3p$ Cl^- states. Both Fowler and Kunz and Van Sciver consider such mixing but since the effect is small, it is not included in their results. Howland and Bassani, Knox, and Fowler include this mixing, and find it to have significant effects in the structure of KCl and

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‡ National Aeronautics and Space Administration fellow in physics.

[1] R. C. Casella, Phys. Rev. **104**, 1260 (1956).

[2] L. P. Howland, Phys. Rev. **109**, 1927 (1958).

[3] A. B. Kunz and W. J. Van Sciver, Phys. Rev. **142**, 462 (1966).

[4] W. Beall Fowler, Phys. Rev. **132**, 1591 (1963).

[5] F. Bassani, R. S. Knox, and W. Beall Fowler, Phys. Rev. **137**, A1217 (1965).