PHYSICAL REVIEW VOLUME 131, NUMBER 2 15 JULY 1963

Electron Paramagnetic Resonance Spectra of Cr^+, Mn^{++}, and Fe^{3+} in Cubic ZnS

REUBEN S. TITLE
T. J. Watson Research Center, International Business Machines Corporation, Yorktown Heights, New York

(Received 7 March 1963)

The paramagnetic spectra of the three ${}^6S_{5/2}$ ions Cr^+, Mn^{++}, and Fe^{3+} have been measured in cubic ZnS. The paramagnetic resonance parameters g, a, and A are compared to the theories for these parameters for the ${}^6S_{5/2}$ state. It is found that the covalent character of the lattice must be taken into account. For the parameter A, a linear relation is found to exist for all three ions between the value of A and the ionicity of the lattice. The extrapolated value of A at 100% ionicity is found to be in agreement with the calculations of Watson and Freeman. The values of g and a are found to be in qualitative agreement with the theories of Watanabe and Gabriel, Johnston and Powell. Exact calculations of the parameters g and a require a detailed knowledge of the environment of the ion.

INTRODUCTION

THE ions Cr^+, Mn^{++}, and Fe^{3+} have a $3d^5$ electron configuration. This configuration is a half-filled d shell and by Hund's rules the ground state of this configuration is ${}^6S_{5/2}$. Because of its spherical symmetry such a state will have no interaction with an electric field. In addition, the magnetic field at the center of the electronic charge distribution will be zero. The state should, therefore, show no hyperfine structure in its spectrum due to an interaction with the magnetic moment of the nucleus. It is well known, however, from paramagnetic measurements on these ions that the ground state is split by a crystalline electric field and that the spectra do have hyperfine structure.

A theoretical explanation for the crystalline field splitting was first given by Watanabe.[1] He suggested that the splitting arises from an admixture into the ${}^6S_{5/2}$ state of other states of the d^5 electron configuration. Such an admixture occurs due to the simultaneous action of the crystalline field, spin-orbit coupling, and spin-spin coupling. The theory has been refined in the case of a cubic field by Gabriel, Johnston, and Powell[2] to take into account not only the quartets as Watanabe did, but also the doublets arising from the $3d^5$ configuration. They have satisfactorily been able to account for the measured cubic field splitting parameter a for Mn^{++} in several ionic crystals.[3,4] Departures from theory are found for crystals showing covalent or partial covalent bonding.[3,5] The theory for D, the axial field splitting parameter, is not in as good agreement with experiment as that for a.[1,6]

The ground states of the Cr^+, Mn^{++}, and Fe^{3+} as previously mentioned also show an anomalous hyperfine structure. The values of A, the hyperfine structure constant, that have been measured for these ions are quite large. Abragam first suggested that this was due to an admixture of the $3s4s3d^5$ configuration into the $3s^23d^5$ configuration.[7] However, an estimate of the admixture by Abragam, Horowitz, and Pryce[8] showed it to be too small to account for the observed hyperfine structure. An explanation that is quantitatively able to explain the hyperfine structure has been given by Heine,[9] Wood and Pratt,[10] and Watson and Freeman.[11] This says that the exchange interaction between the d electrons and paired s electrons in the core is spin orientation dependent. Since the spins of the five d electrons are aligned in the ${}^6S_{5/2}$ state, these electrons will have a different exchange interaction with the electron in an s^2 configuration which has its spin parallel to that of the d electrons than for that which is antiparallel. This causes a polarization of the s^2 configuration which can then produce a magnetic field at the nucleus. Detailed calculations of the polarizations of the $1s^2$, $2s^2$, and $3s^2$ configurations have been made by Watson and Freeman.[11] They have quantitatively been able to account for the observed hyperfine structure of Mn^{++} and Fe^{3+} in ionic crystals.

In this paper results of electron paramagnetic resonance (EPR) measurements on the $3d^5$ electron configurations of Cr^+, Mn^{++}, Fe^{3+} in cubic ZnS are reported and compared to the above theories. This is the first lattice in which all three ions with a $3d^5$ configuration have been observed. The comparison of the results of experiment with the above theories is not completely valid. The theories accounting for both the effects of the crystalline field and the anomalous hyperfine structure are for ionic crystals, whereas ZnS has bonding which is partly covalent.[12] This will be considered in the comparison.

EXPERIMENTS AND RESULTS

The single crystals of cubic ZnS were grown by Jona using a vapor transport method.[13]

---

[1] H. Watanabe, Prog. Theoret. Phys. (Kyoto) **18**, 405 (1957).

[2] J. R. Gabriel, D. F. Johnston, and M. J. D. Powell, Proc. Roy. Soc. (London) **A264**, 503 (1961).

[3] T. P. P. Hall, W. Hayes, and F. I. B. Williams, Proc. Phys. Soc. (London) **A78**, 883 (1961).

[4] Walter M. Walsh, Jr., Phys. Rev. **122**, 762 (1961).

[5] R. S. Title, Phys. Rev. **130**, 17 (1963).

[6] W. J. Nicholson and G. Burns, Phys. Rev. **129**, 2490 (1963).

[7] A. Abragam, Phys. Rev. **79**, 534 (1950).

[8] A. Abragam, J. Horowitz, and M. H. L. Pryce, Proc. Roy. Soc. (London) **A230**, 169 (1955).

[9] V. Heine, Phys. Rev. **107**, 1002 (1957).

[10] J. H. Wood and G. W. Pratt, Jr., Phys. Rev. **107**, 995 (1957).

[11] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).

[12] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd ed.

[13] F. Jona, J. Phys. Chem. Solids **23**, 1719 (1962).

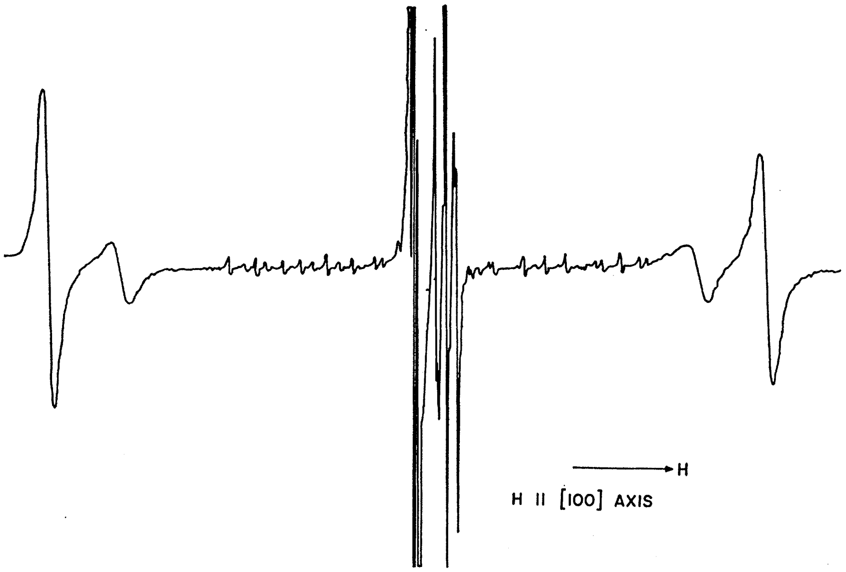

FIG. 1. EPR spectrum of ZnS:Cr$^+$, Mn^{++}, Fe^{3+} with $H\|[100]$ axis.

Paramagnetic measurements were made at liquid-nitrogen temperature using a Varian V-4500 spectrometer with 100 kc/sec modulation. As previously reported,[14,15] the observation of the Cr$^+$ and Fe^{3+} spectra require that the sample be illuminated with 365 mμ radiation. Mn^{++} can be observed either in the dark or in the illuminated sample without any modification in the spectrum.

In one crystal containing all three impurities the three were observed simultaneously as shown in Fig. 1. The spectrum is taken with the magnetic field oriented along the [100] axis of the crystal. The weaker lines seen throughout the center part of the spectrum are due to Mn^{++}. The lines at the highest and lowest fields in Fig. 1 are the fine structure lines of the Fe^{3+} spectrum. The $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition of Fe^{3+} and the entire spectrum of Cr$^+$ occur at the center of Fig. 1. Details of these latter lines are shown in the slower scan of Fig. 2. The iron used for doping was enriched to 50% in Fe^{57}. Fe^{57} has a nuclear spin of $\frac{1}{2}$. The two lines of the hyperfine structure of Fe^{57} appear with the single line due to the even isotopes of iron as the threefold line seen at the left in Fig. 2. The Cr$^+$ spectrum on the right shows the fivefold fine-structure pattern indicated by the arrows in the figure. In addition, the center $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition shows a superhyperfine structure probably due to an interaction with Zn^{67}.[14]

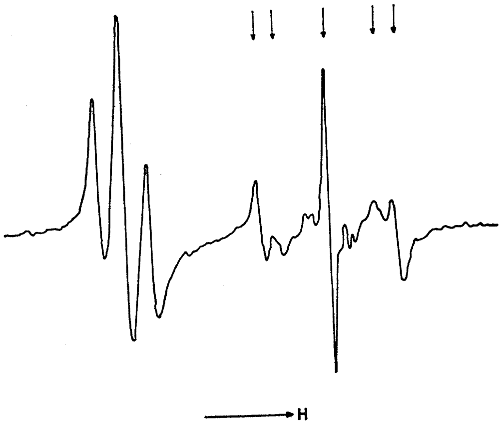

FIG. 2. The center part of the above spectrum.

The paramagnetic data for the three ions are summarized in Table I.

DISCUSSION

The *g* Values

Thd g values of the three ions in Table I are all close to the free-electron value 2.0023. Watanabe[1] had predicted that the admixture of the quartets of the d^5 configuration into the $^6S_{5/2}$ ground state would lead to a deviation from the free-electron value given by $\Delta g=-2\lambda^2/P^2$. The quantity λ is the spin-orbit coupling constant, and P is the energy separation of $3d^{5}\,^4P$ from the $^6S_{5/2}$ ground state. The deviation is always predicted to be negative. Reference to Table I shows that Δg is negative for Cr$^+$ and Mn^{++}, but is positive for Fe^{3+}.

TABLE I. Paramagnetic resonance parameters of the $^6S_{5/2}$ ions in cubic ZnS.

Ion	g	a (10^4 cm^{-1})	A (10^4 cm^{-1})	Ref.
Cr$^+$	1.9995 ±0.0005	3.9 ±0.1	13.4 ±0.1	This paper
Mn^{++}	2.0021	7.97	−63.73	4
Fe^{3+}	2.019 ±0.001	127.4 ±0.5	7.69 ±0.05	This paper

---

[14] J. Dieleman, R. S. Title, and W. V. Smith, Phys. Letters **1**, 334 (1962); R. S. Title, Bull. Am. Phys. Soc. **7**, 88 (1962); A. Rauber and J. Schneider, Z. Naturforsch. **17a**, 266, (1962).

[15] A. Rauber, J. Schneider, and F. Matossi, Z. Naturforsch. **17a**, 654 (1962).

It was, however, shown by Fidone and Stevens[16] that covalency in the bonding of the ion to the lattice also leads to a contribution to Δg. This contribution can be positive and would probably be more pronounced for Fe^{3+} than Cr^+ and Mn^{++}. Quantitative calculation would require a detailed knowledge of the environment of the ion.

The *A* Values

To compare the measured values of A with the calculations by Watson and Freeman[11] of the polarization of the $1s^2$, $2s^2$, and $3s^2$ core electrons, Table II has been constructed. The quantity χ is the magnetic field per spin expressed in atomic units (1 a.u.$=4.21\times10^4$ Oe). The magnetic field at the nucleus H_e produced by the electrons is obtained from the relation $H_e=(AIJ/\mu_n)$, where I is the nuclear spin, $J=\frac{5}{2}$ for the $^6S_{5/2}$ configuration, and μ_n is the nuclear magnetic moment. The calculated value of χ for $(Cr^{53})^+$ is an extrapolation of the χ values calculated by Watson and Freeman for Mn^{++} and Fe^{3+}.

The measured χ_{exp} values are much less than the calculated values. This is again a manifestation of the covalent character of the bonding in ZnS. Van Wieringen[17] had pointed out that the A values of Mn^{++} ions decrease as the covalency of the bonds increases. Recently, Matamura[18] has shown that if the A values of Mn^{++} ions are plotted against the ionicity of the bonds, a linear relation is obtained (Fig. 3). Extrapolating this line to 100% ionicity, a value of $A=100\times10^{-4}$ cm^{-1} is found. This gives a value of $\chi=-3.36$ a.u. which is in excellent agreement with the calculated value of -3.34 a.u.

For $(Fe^{57})^{3+}$, other measurements have been made in MgO and ZnO. In[19] MgO $A=10.1\times10^{-4}$ cm^{-1}, and in ZnO $A=9.02\times10^{-4}$ cm^{-1}.[20] If one assumes that for $Fe^{57})^{3+}$ a linear plot between A and ionicity exists as it does for $(Mn^{55})^{++}$, then the extrapolated value of A of $(Fe^{57})^{3+}$ for 100% ionicity is 11.4×10^{-4} cm^{-1}. (Fig. 4.) This gives a value for $\chi=-2.94$ a.u. which again compares favorably with the calculated value of -3.00 a.u.

TABLE II. The magnetic field at the nucleus of each of the $^6S_{5\,2}$ ions.

Ion	$\lvert A\rvert$ (10^4 cm^{-1})	I	μ_n (nm)	$\lvert H_e\rvert$ (Oe)	$\lvert\chi_{\text{exp}}\rvert$ (a.u.)	χ_{calc} (a.u.)
$(Cr^{53})^+$	13.4	$\frac{3}{2}$	-0.47351	4.17×10^5	1.98	(-3.94)
$(Mn^{55})^{++}$	63.73	$\frac{5}{2}$	$+3.468$	4.50×10^5	2.14	-3.34
$(Fe^{57})^{3+}$	7.69	$\frac{1}{2}$	$+0.0903$	4.17×10^5	1.98	-3.00

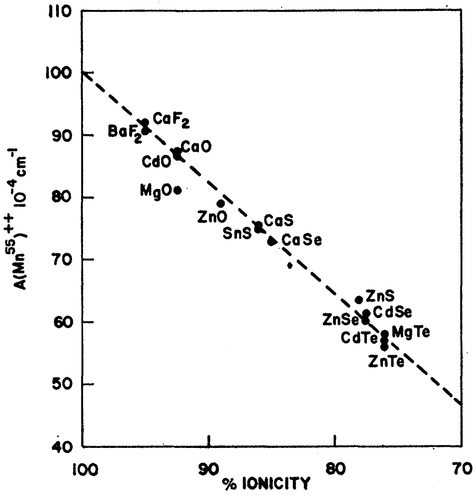

FIG. 3. The value of $A\,(Mn^{55})^{++}$ plotted against the ionicity of the lattice.

For $(Cr^{53})^+$, two other measurements of A have been made. One is in silicon with the Cr^+ in an interstitial position which gave $A=10.67\times10^{-4}$ cm^{-1}.[21] $(Cr^{53})^+$ has also been seen in[22] NaF with $A=14.0\times10^{-4}$ cm^{-1}. The A value for Cr^+ in the highly ionic crystal NaF is not very different than the value of $A=13.4\times10^{-4}$ cm^{-1} measured in ZnS.

A plot of the measured A values of $(Cr^{53})^+$ against the ionicity of the site in the lattice is shown in Fig. 5. The ionicity of the interstitial position in silicon was

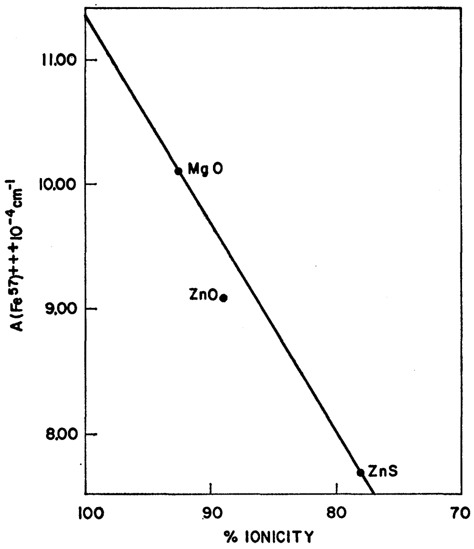

FIG. 4. The value of $A\,(Fe^{57})^{3+}$ plotted against the ionicity of the lattice.

---

[16] I. Fidone and K. W. H. Stevens, Proc. Phys. Soc. (London) **73**, 116 (1959).

[17] J. S. Van Wieringen, Discussions Faraday Soc. **19**, 118 (1955).

[18] On Matamura, J. Phys. Soc. Japan **14**, 108 (1959).

[19] E. S. Rosenvasser and G. Feher, Bull. Am. Phys. Soc. **6**, 117 (1960).

[20] W. M. Walsh, Jr., and L. W. Rupp, Jr., Phys. Rev. **126**, 1952, (1962).

[21] H. H. Woodbury and G. W. Ludwig, Phys. Rev. **117**, 102 (1960).

[22] W. Hayes and D. A. Jones, Proc. Phys. Soc. (London) **71**, 503 (1958).

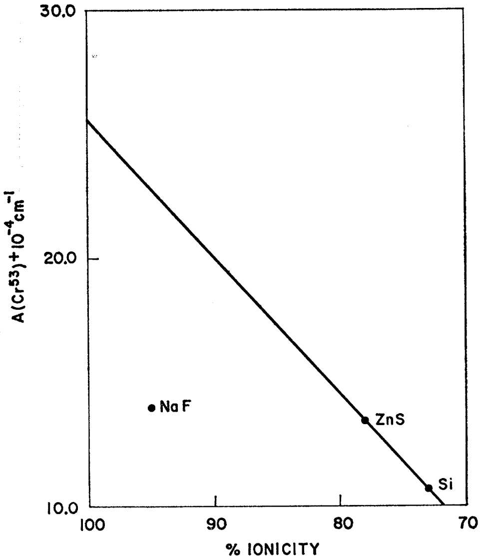

FIG. 5. The value of $A\,(\mathrm{Cr}^{53})^+$ plotted against the ionicity of the lattice.

found first by noting that Cr^+ and Mn^{++} have approximately the same electronegativity.[12] The measured value of $A=-53.47\times10^{-4}$ cm^{-1} for Mn^{++} in the interstitial site in silicon[20] was then used with Fig. 3 to determine the ionicity at 73% for this site. It will be noticed that the three measured A values are not collinear. A straight line drawn through the ZnS and interstitial silicon points gives an extrapolated value of 25.5×10^{-4} cm^{-1} at 100% ionicity. The value of χ derived from this is -3.78 a.u. which is in agreement with the value of -3.94 a.u. extrapolated from the calculations of Watson and Freeman.

The discrepancy in fitting the data using the A value for NaF is not understood. If the ionicity were as large as expected[12] a much larger value of A for $(\mathrm{Cr}^{53})^+$ should have been found in NaF.

In summary, one sees that the A values for $(\mathrm{Cr}^{53})^+$, $(\mathrm{Mn}^{55})^{++}$, and $(\mathrm{Fe}^{57})^{3+}$ in ZnS are much lower than the values Watson and Freeman had calculated for ionic crystals. However, if one assumes that a linear relation exists between A, and the ionicity as Matamura had indeed already found for $(\mathrm{Mn}^{55})^{++}$, then the measured A values in ZnS are found to be in agreement with the results of Watson and Freeman.

The *a* Values

The a values for Mn^{++} in an ionic crystal have been calculated by Gabriel, Johnston, and Powell. For Mn^{++} in a tetrahedral environment as in ZnS a value of a of 0.3×10^{-4} cm^{-1} is calculated. The measured value of 7.97×10^{-4} cm^{-1} is more than an order of magnitude larger. The discrepancy is again due to the covalent character of the bonds in ZnS. In fact, there is a regular though not linear relation between the value of a for Mn^{++} and the degree of covalency in the II-VI zinc-blended and wurtzite compounds[5] (Fig. 6). The hexagonal wurtzite crystals have been included in Fig. 6 since they show a cubic term in the interaction of the ion with the crystalline field. In the case of ZnS, where a has been measured in both cubic and hexagonal modifications, the values of a agree with each other within the experimental errors. Although there is much less data, the a values of Cr^+ and Fe^{3+} also increase markedly as the ionicity of the lattice is decreased.

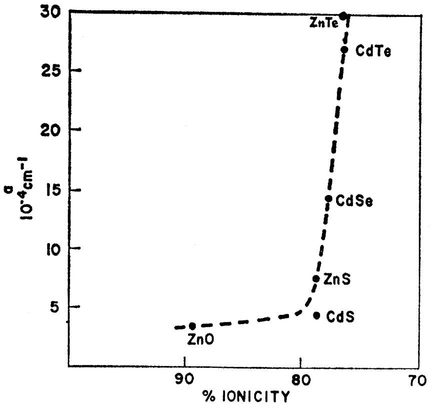

FIG. 6. A plot of cubic field splitting parameter a against the ionicity of the lattice.

In absence of a theory on how covalency affects the a value, it is rather difficult to compare the relative a values of Cr^+, Mn^{++}, and Fe^{3+} in ZnS. For an ionic crystal, Gabriel, Johnston, and Powell have shown that a is proportional to $\lambda^4(Dq)^n$ where λ is the spin-orbit coupling constant, Dq a measure of the crystalline field strength, and n varies between 3.5 and 6.

If one assumes that the effects of the covalency are the same for Cr^+, Mn^{++}, and Fe^{3+}, i.e., Dq increases by the same factor from its original value in all three ions then the relative values of a for the three ions in ZnS should be related to $\lambda^4(Dq)^n$, where λ and Dq are the ionic crystal values. These values have not been measured for all three ions. If one interpolates the values of λ and Dq that have been measured (as recorded for example in the tables in McClure's article[23]) one finds that the relative values of a as measured for Cr^+, Mn^{++}, and Fe^{3+} in ZnS can be satisfactorily accounted for as to their relative order of magnitude.

SUMMARY

The resonance parameters of the three ${}^6S_{5/2}$ ions Cr^+, Mn^{++}, Fe^{3+} in ZnS are all affected by the covalent character of the bonds. In the case of the hyperfine structure constant A, a linear relation exists between the value of

---

[23] D. S. McClure, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 399.

A and the ionicity of the lattice at the impurity site. As far as the g values and the a values are concerned, quantitative estimates of the effects of covalency require an accurate knowledge of the environment of the ion.

ACKNOWLEDGMENTS

I wish to acknowledge the interest of Dr. R. W. Keyes in this research. I also would like to thank Dr. F. Jona for growing the crystals and E. Tynan for aid in taking the paramagnetic data.

PHYSICAL REVIEW VOLUME 131, NUMBER 2 15 JULY 1963

Junction Potential Studies in Tunnel Diodes

W. Bernard, H. Roth, A. P. Schmid, and P. Zeldes
Raytheon Research Division, Waltham, Massachusetts

(Received 18 February 1963)

A unique model is proposed for the potential distribution in the junction region of a tunnel diode. The essential feature of this model, in addition to band tailing, is a discontinuity in the band edges at the n-p interface arising from a difference in the electron affinities of degenerate n- and p-type semiconductors. In connection with the proposed description of a tunnel diode junction, precise capacitance measurements have been carried out on a series of germanium units at 78°K. The experimentally determined values of the capacitance built-in voltage are in substantial agreement with the theoretical prediction, $eV_b = E_{g0} + \frac{1}{5}(\xi_n + \xi_p)$, and thus lend strong support to the validity of the discontinuity model. The temperature dependence of the built-in voltage is also discussed.

MANY fundamental properties of the tunnel diode can be reasonably well explained on the basis of a degenerate semiconductor model in which the intrinsic energy band structure is retained, the appropriate conducting band simply being filled to degeneracy by the addition of a large concentration of suitable impurity atoms. Using this band picture it is possible, for example, to account for the essential behavior of the current-voltage characteristic, including the negative resistance,[1,2] the existence of phonon-assisted processes,[3,4] and the pressure[5] and magnetic field[6] dependences. Further, by introducing into the forbidden band gap energy levels appropriate to deep-lying impurities[7] and lattice defects[8] one can account in large measure for the excess current observed at increased forward bias.

However, it seems clear that further progress in understanding the various properties exhibited by tunnel diodes requires the adoption of a more realistic description of degenerate semiconductors. Pankove's optical studies, both on bulk germanium[9] and germanium tunnel diode junctions,[10] first suggested the inadequacy of the conventional energy-band description. More recently, Sommers[11] and Meyerhofer and his coworkers[12] have made a systematic study of the electrical properties of germanium junctions and interpreted a large variety of data in terms of existing theories. They cannot, however, account for the built-in potential determined from junction capacitance measurements. Whereas the conventional junction model predicts a capacitance built-in potential considerably in excess of the band gap, previous experimental results, obtained at room temperature, have yielded values consistently lower than the band gap.

The correct interpretation of the degenerate band structure must lead to a clarification of the junction-capacitance anomaly. In this note we propose a unique model of the potential distribution in the junction region of a tunnel diode. The essential feature of this model, which is based on fundamental considerations, is a discontinuity in the band edges at the n-p interface of the junction. The results of a series of precise junction capacitance measurements performed at 78°K are presented and compared with predictions based on the discontinuity model. The temperature dependence of the capacitance built-in voltage is also discussed.

The modifications which occur in the energy band spectrum of a semiconductor when extremely high concentrations of simple donor or acceptor impurities are added can be visualized in the following way. At low impurity concentrations, each additional impurity merely removes a conducting state from the edge of the conduction (or valence) band and replaces it with a set of

---

[1] L. Esaki, Phys. Rev. **109**, 603 (1959).

[2] E. O. Kane, J. Appl. Phys. **32**, 83 (1961).

[3] L. V. Keldysh, Zh. Eksperim. i Teor. Fiz. **34**, 962 (1958) [translation: Soviet Phys.—JETP **7**, 665 (1958)].

[4] N. Holanyak, I. A. Lesk, R. N. Hall, J. J. Tiemann, and H. Ehrenreich, Phys. Rev. Letters **3**, 167 (1959).

[5] S. L. Miller, M. I. Nathan, and A. C. Smith, Phys. Rev. Letters **4**, 60 (1960).

[6] A. R. Calawa, R. H. Rediker, B. Lax, and A. L. McWhorter, Phys. Rev. Letters **5**, 55 (1960).

[7] C. T. Sah, Phys. Rev. **123**, 1594 (1961).

[8] A. G. Chynoweth, W. L. Feldman, and R. A. Logan, Phys. Rev. **121**, 684 (1961); R. S. Claassen, J. Appl. Phys. **32**, 2372 (1961).

[9] J. I. Pankove, Phys. Rev. Letters **4**, 454 (1960).

[10] J. I. Pankove, Phys. Rev. Letters **4**, 20 (1960).

[11] H. S. Sommers, Jr., Phys. Rev. **124**, 1101 (1961).

[12] D. Meyerhofer, G. A. Brown, and H. S. Sommers, Jr., Phys. Rev. **126**, 1329 (1962).