

From this the following conclusions may be drawn:

(1) By calculating the zero-point energies and motions of these modes as in reference 3, the next higher-order corrections to the B.C.S. theory could be obtained. We justify this theory in that we show that these reasonably large corrections do not change the excitation spectrum in essentials.

(2) Collective and plasma effects indeed reinforce the B.C.S. theory in the way predicted in reference 1, even though the exact matrix elements in B.C.S. are incorrect because of the neglect of collective effects.

I am indebted to H. Suhl for help with some of the calculations and for many conversations. A more complete description of the method will be published later.

<sup>1</sup> P. W. Anderson, Phys. Rev. **110**, 985 (1958), this issue.

<sup>2</sup> Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957). This is called B.C.S. hereafter.

<sup>3</sup> K. Sawada, Phys. Rev. **106**, 372 (1957); Sawada, Brueckner, Fukuda, and Brout, Phys. Rev. **108**, 507 (1957); R. Brout, Phys. Rev. **108**, 515 (1957).

<sup>4</sup> This is related to a method used by D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953), Appendix II.

<sup>5</sup> M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957).

<sup>6</sup> N. N. Bogoliubov, J. Exptl. Theoret. Phys. U.S.S.R. (to be published). Similar relations were also derived by J. G. Valatin (private communication via J. Bardeen).

<sup>7</sup> By Feynman's argument [see reference 1; also Phys. Rev. **94**, 262 (1954)], this implies that zero-point motions greatly reduce the long-range correlation in the Bardeen theory.

### Sign of the Cubic Field Splitting for $Mn^{++}$ in ZnS

G. D. WATKINS

General Electric Research Laboratory, Schenectady, New York

(Received April 1, 1958)

THE electron spin resonance of  $Mn^{++}$  in cubic ZnS has been studied by Matarrese and Kikuchi.<sup>1</sup> They report that in the spin Hamiltonian

$$H = g\beta\mathbf{H} \cdot \mathbf{S} + \frac{1}{6}a(S_x^4 + S_y^4 + S_z^4) + A\mathbf{I} \cdot \mathbf{S},$$

one has  $a = -8.35 \pm 0.06$  gauss and  $A = +68.4 \pm 0.1$  gauss. Actually, since the measurements were made at room temperature, a change of sign for both the cubic field splitting constant  $a$  and the hyperfine interaction constant  $A$  would also produce the same spectrum. In order to distinguish between the two possibilities, it is necessary to measure the relative intensities of the transitions at low temperature.<sup>2</sup> We have made such a measurement<sup>3</sup> at 4°K and at a frequency of 20 kMc/sec, and find that the signs reported were in error. They should be  $a = +8.35 \pm 0.06$  gauss,  $A = -68.4 \pm 0.1$  gauss.

This is of interest because of a recent theoretical treatment of  $Mn^{++}$  in cubic fields by Watanabe.<sup>4</sup> He concludes that  $a$  should be positive regardless of the sign of  $D$  in the cubic potential  $-eV = D(x^4 + y^4 + z^4 - \frac{2}{3}r^4)$ .

Most measurements for manganese have been in solids where the ion is surrounded by six negative ions in approximate octahedral symmetry. In these solids  $D$  is positive, and the sign of  $a$  has been found to be positive also.<sup>5</sup> In ZnS, the ion is presumed to be surrounded by a tetrahedron of four negative sulfur ions and the sign of  $D$  would therefore be negative. As a result, this system provides an important test for the theory, and the positive sign for  $a$  appears to confirm Watanabe's result. Similar agreement has been found for manganese in germanium, where the sign of  $a$  has also been determined to be positive.<sup>6</sup>

However, the crystalline model does not predict the correct sign of the  $g$  shift in these substantially covalent solids. Watanabe's result states that the  $g$  value should always be less than the free electron value (2.0023). The measured values are  $2.0025 \pm 0.0002$  in ZnS<sup>1</sup> and  $2.0061 \pm 0.0002$  in germanium.<sup>6</sup> Positive  $g$  shifts are also indicated in powders of CdS, ZnSe, and CdTe.<sup>7</sup> As a result, the agreement in the sign of  $a$  does not necessarily indicate that the crystalline field model can be successfully applied to such highly covalent solids.

<sup>1</sup> L. M. Matarrese and C. Kikuchi, J. Phys. Chem. Solids **1**, 117 (1956).

<sup>2</sup> See, for instance, W. Low, Phys. Rev. **105**, 793 (1957).

<sup>3</sup> The crystal used for this measurement was kindly supplied by Professor Kikuchi.

<sup>4</sup> H. Watanabe, Progr. Theoret. Phys. Japan **18**, 405 (1957).

<sup>5</sup> K. D. Bowers and J. Owen, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 342.

<sup>6</sup> G. D. Watkins, Bull. Am. Phys. Soc. Ser. II, **2**, 345 (1957).

<sup>7</sup> J. S. VanWieringen, *Discussians Faraday Soc.* **19**, 118 (1955).

### Rate Processes and Low-Temperature Electrical Conduction in $n$ -Type Germanium

SEYMOUR H. KOENIG

International Business Machines Watson Laboratory at  
Columbia University, New York, New York

(Received March 17, 1958)

THE low-temperature electrical conduction of  $n$ -type germanium as a function of applied electric field is characterized by an ohmic region for fields less than  $\sim 0.2$  v/cm, a region of steadily increasing conductivity, and finally a critical "breakdown" field at which the current rises "vertically" with the applied electrical field.<sup>1</sup> The large variation of conductivity is due mainly to an increase in carrier density as, with increasing electric field, the mean carrier energy increases from its equilibrium value. The breakdown is associated, in a general way, with ionization of neutral donors by the impact of "hot" electrons.<sup>1</sup> In Fig. 1, data obtained by pulse techniques are presented to illustrate the behavior at high current densities.<sup>2</sup> The essential feature to be noted is that after a significant "vertical" rise the  $j$ - $E$  curve becomes concave downwards.