Anomalous Photovoltaic Effect in ZnS Single Crystals

A. LEMPICKI

Research Laboratories, Sylvania Electric Products Incorporated, Bayside, New York

Larger-than-band-gap photovoltages have been observed in both cubic and hexagonal crystals of ZnS with stacking faults. Under monochromatic excitation the photovoltage measured parallel to the c axis shows two sign reversals at about 3300 A and 3500 A and peaks at approximately 3250 A and 3400 A. The position of the 3400 A peak shifts by $\sim$70 A depending on the crystal structure. In the direction perpendicular to the c axis the photovoltage does not change sign and remains smaller than the band gap. Hexagonal crystals free of stacking faults do not show anomalous photovoltages. Heat treatment causes appearance of both. A pyroelectric polarization is found to be correlated with the sign of photovoltage.

INTRODUCTION

LARGER–THAN–BAND–GAP photovoltages have been recently observed on films of CdTe by Pensak[1] and Goldstein[2] and on single crystals of ZnS by Ellis et al.[3] and Cheroff and Keller.[4] In some cases the voltages are of the order of 100 volts or more for crystals a few millimeters long. Cheroff and Keller found that both the magnitude and the sign of photovoltage depend upon the wavelength of exciting light. Although it has been suggested that the magnitude of the photovoltage can be explained by postulating p-n junctions connected like batteries in series[2] or other types of barriers associated with the crystallographic disorder,[3,5] direct experimental evidence for it was lacking. Moreover, these hypotheses offer no explanation of the reversal of sign.

In this paper we shall present more experimental data obtained on various ZnS crystals. The basic phenomenon is still not understood. We feel, however, that some new information has been gained in establishing a connection between crystal disorder and the photovoltage.

EXPERIMENTAL

All measurements were made with monochromatic light obtained from a high-pressure Xe arc and a Hilger D121 double monochromator. The excitation energy at the sample is given in Fig. 1. The crystals were mounted with silver-paint electrodes on polystyrene plates and placed in a chamber through which dry nitrogen was passing continuously.

The short-circuit current (I_{sc}) through the crystals was measured by a vibrating reed electrometer. Since the shunt resistance of the electrometer was considerably lower than the crystal resistance, the time constant of the circuit was sufficiently low to use an automatic drive of the monochromator. The short-circuit current was directly displayed as a function of wavelength on a recorder driven by the electrometer. The measurement

of open-circuit voltage (V_{oc}) is more difficult. Attempts to measure it directly with an open-circuit electrometer lead to very long time constants (high resistance of the crystals). A bucking circuit was therefore used with the electrometer as null instrument. These measurements were made point by point. In some crystals the out-of-balance voltage applied by the bucking circuit produced slow drifts of the null point. The direction of drift depends upon the polarity of the out-of-balance voltage. This effect is probably caused by some slow space charge readjustment. For this reason we consider I_{sc} as a more reliable and reproducible quantity for locating peak positions. In agreement with the results of Cheroff and Keller, it was found that V_{oc} saturates at quite low intensities and hence no correction for equal excitation intensity is necessary. I_{sc} varies linearly with intensity and therefore should be corrected. Since in all experiments the excitation was the same and the results are used only for comparing different samples the correction was not applied.

For the study of pyroelectric current we used a method developed by Chynoweth[6] and applied by him to barium titanate and other substances. The vibrating reed electrometer is connected directly across the crystal (shunt resistance 10^{10} ohms–10^{12} ohms). The
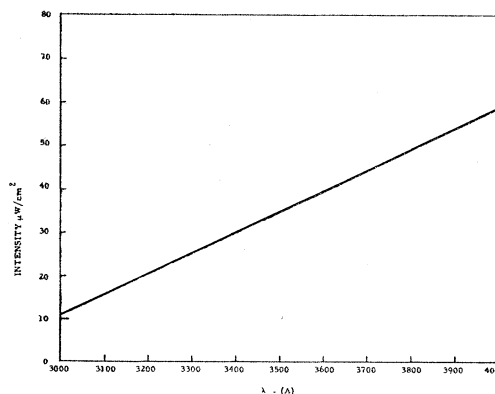

FIG. 1. Excitation energy at the sample vs wavelength.

[1] L. Pensak, Phys. Rev. 109, 601 (1958).
[2] B. Goldstein, Phys. Rev. 109, 601 (1958).
[3] S. G. Ellis et al., Phys. Rev. 109, 1860 (1958).
[4] G. Cheroff and P. Keller, Phys. Rev. 111, 98 (1958).
[5] W. J. Merz, Helv. Phys. Acta 31, 625 (1958).

[6] A. G. Chynoweth, J. Appl. Phys. 27, 78 (1956); Acta Cryst. 10, 705 (1956); Phys. Rev. 102, 705 (1956).

TABLE I. Characteristic of the ZnS specimens.

Sample	Length (mm)	Structure	Birefringence	I_{sc} Extrema (A)	Sign reversals (A)	Peak V_{oc} (v)	Fluorescence color
1	2.36	Hex	Uniform	3270	None	0.5	Blue
2	3.84	Hex	Uniform	3285	None	0.8	Green
3	3.13	Hex-very light smear	Few bands	3250	None	0.05	Blue
4	1.0	...	Few bands	3300	None	0.1	Green
5	2.9	Hex-very light smear	Few bands	3250	None	0.45	Blue
6	2.88	Hex-light smear	Banded	(3480) 3285	3480 3330	0.18	Green
7	3.9	Hex-light smear	Banded	(3470)	None	0.06	Blue
8	0.93	Hex-medium smear Trace of cubic	Banded	(3450) 3275	3600 3370	6	Green
9	3.9	Mixture hex and cubic smeared	Banded	(3450) 3250	3320	19	Blue-green
10	3.4	Mixture hex and cubic smeared	Banded	(3425) 3250	3430	0.5	Blue
11	1.68	Mixture hex and cubic and 6-layer smeared	Banded	(3405) 3230	3510 3335	5.5	Blue-green
12	7.16	Mixture hex and cubic smeared	Banded	(3410) 3280	3485 3335	1.4	Blue
13	2.33	Cubic smeared	Banded	(3420) 3250	3515 3285	9	Blue
14	12.0	Cubic smeared	Banded	(3400) 3250	3510 3325	90	Blue
15	1.2	Cubic smeared	Banded	(3395) 3250	3480 3330	3.4	Blue
16	1.0	Cubic smeared	Banded	(3390) 3290	3470 3340	0.4	Blue

crystal is then heated by a square pulse of infrared and the current observed. The radiation was obtained from a tungsten ribbon lamp through a Corning 2540 filter. A photographic shutter was used to produce single pulses of infrared.

RESULTS

The crystals used for this study were grown by Dr. H. Samelson of our laboratories by a vapor phase method. The starting material was RCA luminescent grade powder. This was first degassed at 800°C and 10^{-5} mm Hg for about 1 hr to reduce the Cl content below 0.02%. The growth then took place in sealed tubes in an atmosphere of H_2S (10 mm Hg at room temperature) at temperatures between 1100°C and 1230°C. No impurities were added.

In general, there is little uniformity among the crystals in one batch. Their shape, structure, optical properties, and photovoltaic properties can vary widely. The florescence was pale blue or green.

A number of crystals were selected from four growth batches and subject to the following examination: (1) x-ray structure determination, (2) observation of birefringence in a polarizing microscope, and (3) measurement of I_{sc} and V_{oc} in the range 3000 A to 4000 A.

On the basis of structure determination the crystals were divided into 3 groups (Table I). Samples 1 to 7

are hexagonal. The amount of smearing of certain x-ray diffraction spots, indicating stacking reversals,[7] increases down this sequence. The first two samples are free of any indication of disorder.

As has recently been reported,[8] most synthetic crystals (both hexagonal and cubic) show bands of different birefringence more or less sharply separated by planes perpendicular to the c axis. Crystals which show uniform birefringence (specimens 1 and 2) show no smearing of x-ray spots.

Crystals 8 to 12 are of mixed structure. Both cubic and hexagonal spots appear on the films and both are smeared. It is difficult to arrange this group in a sequence of increasing disorder because in general the crystals are not uniform in structure along their length. The sequence adopted is only a rough estimate.

The last group of crystals (13 to 16) has cubic structure. All of them show smearing of diffraction spots. Cubic specimens of the same degree of perfection as the hexagonal ones were not available. Both the mixed and the cubic group show typical birefringence banding.

In order to compare the photovoltaic measurements, we have used a sign convention essentially similar to that of Cheroff and Keller. The I_{sc} peak well inside the fundamental absorption region ($\lambda < 3300$ A) is called

[7] L. Strock and V. A. Brophy, Am. Mineralogist 40, 94 (1955).
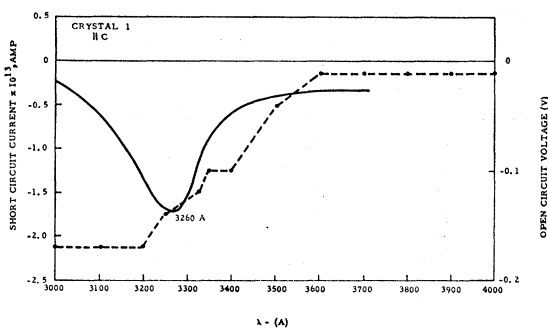[8] L. W. Strock, Acta Cryst. 10, 840 (1957).

FIG. 2. V_{oc} (broken line) and I_{sc} (continuous line) vs wavelength.

negative and the peak at longer wavelength positive. If the specimen shows only one peak and no reversal of sign we call it positive or negative depending on the wavelength. The wavelengths of positive peaks are given in parentheses in Table I.

It has been reported[3,5] that under polychromatic excitations there exist a unique correlation between the sign of the photovoltage and the direction of growth of the crystals, the last-to-grow end of the crystal being negative. In our experiments, however, we found that in those crystals where the growth direction could be identified there was no correlation with the sign of the photovoltage. In Table I we give a summary of the photovoltaic measurements made parallel to the c axis (electrodes perpendicular to c).

Figure 2 gives the I_{sc} and V_{oc} for crystal 1. It is seen that there is no reversal of sign and only the negative peak is present. It is located at 3260 A, hence approximately at the edge of the fundamental absorption.[9-11] The magnitude of V_{oc} is well below the band gap. Such a result would be expected for virtually any semiconductor or insulator in contact with a metal. Crystal 2 shows the same type of a curve. When a small amount of disorder is present (crystals 3, 4, and 5) the results are very nearly the same.

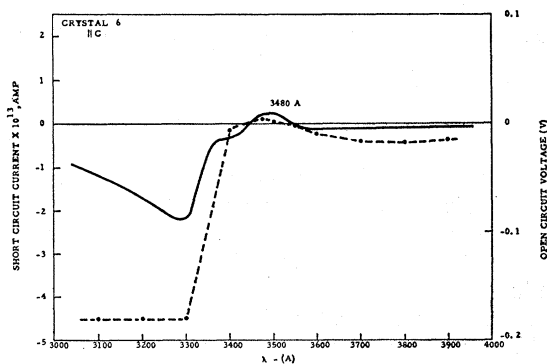The first anomaly in the spectral distribution is

FIG. 3. V_{oc} (broken line) and I_{sc} (continuous line) vs wavelength.

[9] E. A. Kroger, Physica 7, 1 (1940).
[10] C. K. Coogan, Proc. Phys. Soc. (London) B76, 845 (1957).
[11] Piper, Marple, and Johnson, Phys. Rev. 110, 323 (1958).

obtained with crystal 6 (Fig. 3). At short wavelengths the behavior is similar to that of the perfect crystals. At longer wavelengths the positive peak (3480 A) begins to appear. The next specimen (crystal 7, Fig. 4) shows only the positive peak and no sign reversals. It seems that under certain conditions (see heat-treatment experiment) the positive peak completely swamps the negative branch. Notice also that the resistance (V_{oc}/I_{sc}) of crystal 7 is roughly two orders of magnitude lower than that of crystal 6. Beginning with crystal 8 we have examples of truly mixed hexagonal and cubic structures. The V_{oc} becomes larger than the band gap. It is worth noticing that the positive peak shifts towards shorter wavelength (3450 A–3410 A) as the cubic phase becomes more prominent. Crystal 13 is the first one showing smeared 3-layer spots only. Results for a typical member of this group is illustrated on Fig. 5. The curves are very similar to those reported in reference 4. Again we will notice that the positive peak
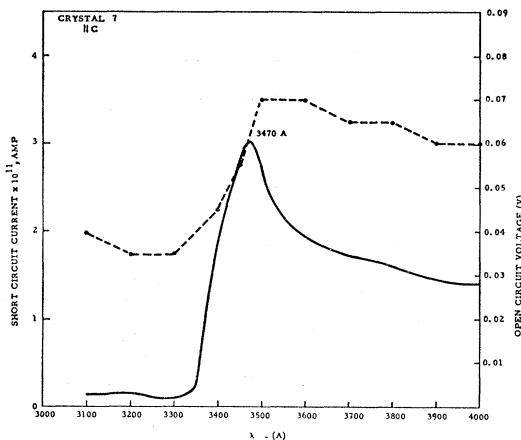

FIG. 4. V_{oc} (broken line) and I_{sc} (continuous line) vs wavelength.

in these predominantly cubic crystals are located at shorter wavelength (3395 A–3425 A) than the corresponding peaks in the predominantly hexagonal material.

We now consider the effect of crystal orientation on the photovoltaic effect. The experiments were conducted on plate-like crystals with the c axis in the plane of the plate and of comparable side dimensions. Results of measurements parallel to the c axis made on crystal 13 are shown on Fig. 6. We see that the shape of both curves are radically different from those of Fig. 5. There are no sign reversals and the magnitude of V_{oc} is lower than the band gap. I_{sc} is in general larger for the perpendicular orientation which is in agreement with the large anisotropy of conductivity reported previously.[12]

As seen in Table I, no correlation of the photovoltaic effect with the fluorescence color of the crystals is apparent.

[12] Lempicki, Frankl, and Brophy, Phys. Rev. 107, 1238 (1957).

HEAT-TREATMENT EXPERIMENT

It has been shown by Strock *et al.*[13] that crystallographic disorder and birefringence banding can be introduced into hexagonal crystals by light heat treatment (150°C–200°C). Small pressure exerted by handling with tweezers can also produce permanent birefringence bands.[14]

To check the effect of heat treatment on photovoltage an initially perfect hexagonal specimen (crystal 2) was heated at 400°C for 30 minutes. The results before the heat treatment are given in Fig. 7(A). They are very similar to those obtained with specimen 1 (Fig. 2). After heating, the results are as given on Fig. 7(B). We see that the sign of the photovoltage has changed, a pronounced positive peak has appeared, and the magnitudes of both the V_{oc} and I_{sc} have increased considerably. The curves are now quite similar to those obtained with a disordered crystal such as No. 7, Fig. 4. The structure of the crystal after heat treatment
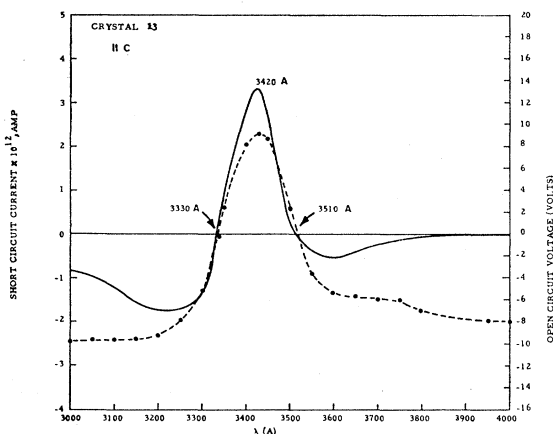

FIG. 5. V_{oc} (broken line) and I_{sc} (continuous line) *vs* wavelength.

showed predominantly 2-layer stacking but with considerable smearing of the diffraction spots. Birefringence bands were also clearly visible. Similar results were obtained by heat treating another perfect hexagonal specimen. It is of interest to note that the highly perfect hexagonal crystals are almost free from surface striations. As soon as birefringence banding is introduced, these fine striations appear. They do not coincide with the band boundaries and are usually on a finer scale.

THE PYROELECTRIC EFFECT

The existence of larger-than-band-gap photovoltages (not attributable to contacts) defines a certain direction in the crystal. It is of interest to correlate it with some other directional property of ZnS. A measurement of

[13] Strock, Brophy, and Peters, Enlarged Abstracts Electrochemical Society Spring Meeting, New York, 1958 (unpublished), p. 61.
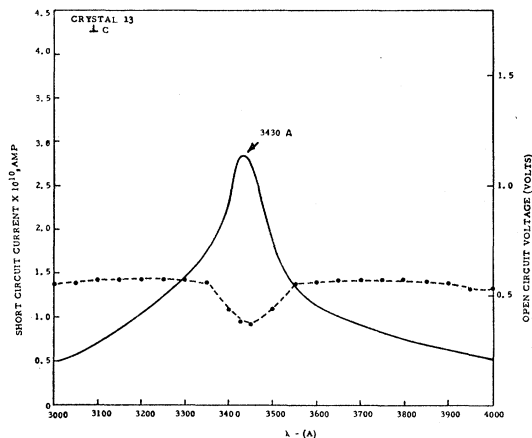[14] G. Neumark (private communication).

FIG. 6. V_{oc} (broken line) and I_{sc} (continuous line) *vs* wavelength.

the piezoelectric effect would be an obvious choice but an experimentally much easier procedure is to look for the existence of a pyroelectric effect. One would expect that all crystals used in this work should show pyroelectric behavior, since all possess a unique axis of symmetry. In the hexagonal crystals this is the c axis and in the disordered, mixed, and cubic crystals, the axis perpendicular to the stacking fault planes. What is usually measured is the so-called secondary or constant-stress pyroelectric effect. Under the conditions of the experiment, the crystal is allowed to expand on heating and thus the change of polarization is produced by both piezo- and pyroelectric components. Since the current is proportional to the rate of change of polarization P it can be written in the form

$$i \propto (\partial P/\partial T)_{\text{stress}}(dT/dt),$$

where T is the temperature and t the time. The shape of the current pulse which one would expect from this expression agrees well with the experimentally observed data (Fig. 8). The pyroelectric current first rises abruptly because the initial rate of heating is large.
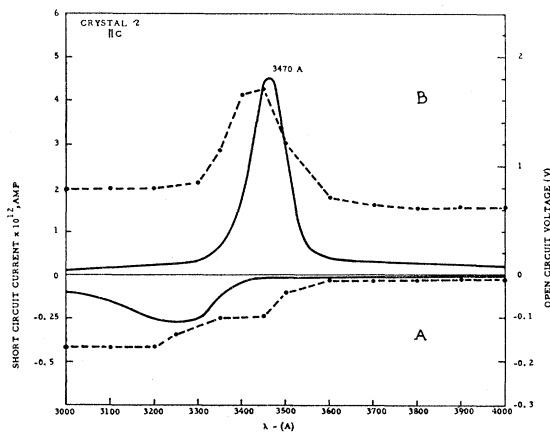

FIG. 7. V_{oc} (broken line) and I_{sc} (continuous line) *vs* wavelength. A—before heat treatment, B—after heat treatment.
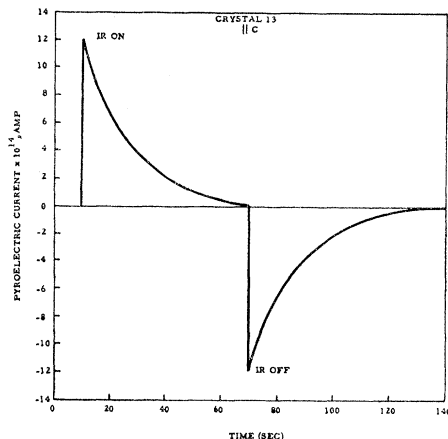
FIG. 8. Pyroelectric current.

It then decays to zero at a rate determined by the thermal relaxation of the specimen. The process is reversed when the heating radiation is turned off.[15] The most important reasons for attributing this behavior to a pyroelectric effect are as follows. First, the current decays to zero during the pulse and hence cannot be due to a photovoltaic contribution. Second, the experiment can be repeated over and over again without any sign of exhaustion. This rules out the action of trapped charges.

We have found that there is a definite correlation between the direction of the pyroelectric current and the positive photovoltaic peak. *The end of the crystal that becomes positive under a 3400 A irradiation also becomes positive when the heating pulse is turned on.*

Crystals which do not show the positive peak (hexagonal with little or no disorder) do not show the pyroelectric current. This is a remarkable result because the ideal hexagonal structure should possess a pyroelectric coefficient.

We have also looked for pyroelectric currents in a direction perpendicular to the *c* axis. This was only possible in a few plate-like specimens. A trace of an effect considerably weaker than that for the parallel orientation was found.

DISCUSSION

The experiments described in this paper do not provide an explanation of either the magnitude or the spectral distribution of the photovoltage. To explain the sign reversals one has to postulate the existance of opposing electric fields with different spectral depend-

---

[15] If the crystal is mounted so that we measure the effect parallel to the *c* axis, it is only important that the rate of heating be uniform along this direction. For such an orientation the second-rank tensor relating polarization to temperature gradient will have only diagonal components. The existence of temperature gradients in other than the *c* direction will not affect the results. It is easy to check for the absence of temperature gradients (tertiary pyroelectric effect) by simply reversing the crystal in its holder. The signal should then be reversed in sign but otherwise unchanged.

ence. Our understanding of the microscopic structure is insufficient to propose a model. The following facts have, however, been established:

(a) The anomalous photovoltaic effect is connected with crystalline disorder and most probably with stacking faults. This follows from its absence in perfect crystals, its appearance after the introduction of disorder, and its dependence on orientation.

(b) The position of the positive peak depends upon the predominant structure present. It is of interest to note, that according to data obtained by Kröger,[9] the edge of the fundamental absorption occurs at 3410 A in cubic material and at 3350 A in hexagonal. In our experiments the positive peak shifts from about 3400 A for predominantly cubic crystals to about 3470 A for predominantly hexagonal crystals. The shift is thus opposite to that of the band edge. Since this peak occurs only in disordered crystals one would be tempted to attribute it to some localized regions of the crystal. If a stacking sequence reversal is the main element of disorder, then it introduces a layer of hexagonal material into a predominantly cubic crystal and vice versa. Thus the peak shift could be characteristic of hexagonal inclusions in cubic structure and cubic inclusions in hexagonal structure. The direction of the shift would then be in agreement with the band gap change.

(c) Crystals which show disorder give rise to a pyroelectric current on heating and there exists a correlation between the direction of this current and the photovoltage. The fact that only disordered crystals show the effect may be due to several causes. First, it is not known whether the pyro- and piezoelectric contributions to the secondary effect in perfect hexagonal structures add or subtract. It is conceivable that they may cancel out. More probable is a second possibility based on the work of Birman,[16] who proposed an explanation for the anomalous birefringence of ZnS. In his model each band of birefringence is a domain of uniform polarization and strain. Since in our experiments we measure only the rate of change of polarization, we cannot conclude anything about the existence of spontaneous polarization in the domains. It is quite possible, however, that $(\partial P/\partial T)$ is larger in strained structures than in a perfect lattice.

If birefringence bands correspond to spontaneously polarized domains, it would be of great interest to find whether the direct of polarization is unique or random. The experiment of Coster, Knol, and Prins[17] quoted in reference 3 tends to indicate that the polar axis has the same direction throughout the whole crystal. The existence of pyroelectric currents establishes only a correlation between photovoltage and the *net change* of polarization. On the other hand, it can be seen from Table I that crystals of roughly equal lengths and equal amounts of disorder can have quite different

---

[16] J. L. Birman (unpublished manuscript, 1957).
[17] Coster, Knol, and Prins, Z. Physik **63**, 345 (1930).

photovoltages. It is difficult to reconcile this with the opinion expressed in reference 3 that all individual elements contributing to the total photovoltage are lined up in one direction.

From Figs. 2, 4, and 7 we see that the negative and positive peaks can occur separately. This suggests that they may be due to independent mechanisms. For the positive peak, processes occurring in the bulk of the crystal are likely to be of major importance. The negative peak, occurring in the region of very high optical absorption, may be mostly governed by surface properties. It is also significant that whenever a crystal shows an abnormally large photovoltage both the negative and positive peaks are of the same order of magnitude. This shows that the mechanism responsible for the larger-than-band-gap voltages must be operative both in the bulk and at or near the surface.

In conclusion we should like to point out that the measurement of the anomalous photovoltaic effect can become a useful tool in the study of crystalline disorder in ZnS. Even at the present stage we can determine from the shape of the I_{sc} curve the predominant crystal structure and the presence of stacking faults. In order to put the correlation between disorder and photovoltaic effect on a more quantitative basis a much deeper understanding of both is necessary. We hope to continue these studies.

ACKNOWLEDGMENTS

Penetration Depth in Impure Superconductors

Peter B. Miller

Department of Physics, University of Illinois, Urbana, Illinois

(Received October 17, 1958)

The equation giving the current density as a functional of the vector potential for an impurity superconductor derived by Mattis and Bardeen is used to compute the temperature dependence of the penetration depth of impure superconductors. Results of calculations for different values of the ratio of the coherence distance to the mean free path and also for different values of the ratio of the coherence distance to the London penetration depth are given. The results are applied to tin as an example, and appreciable deviations from the $[1-(T/T_c)^4]^{-\frac{1}{2}}$ temperature dependence of the penetration depth are found for all values of the mean free path.

PIPPARD'S[1] experiments on penetration depths in tin-indium alloys show that there is a marked increase in penetration depth with decrease in the mean free path, l, from impurity scattering. Largely on the basis of this work, Pippard suggested that the London equation for the current density in terms of the vector potential,

$$\mathbf{j}(\mathbf{r}) = -(1/c\Lambda)\mathbf{A}(\mathbf{r}), \qquad (1)$$

be replaced by the nonlocal relation

$$\mathbf{j}(\mathbf{r}) = \frac{-3}{4\pi c\Lambda(T)\xi_0} \int \frac{\mathbf{R}\mathbf{R}\cdot\mathbf{A}(\mathbf{r}')J(R,T)e^{-R/l}}{R^4} d\mathbf{r}', \quad (2)$$

where $\mathbf{R}=\mathbf{r}-\mathbf{r}'$, $\Lambda(T)$ is the London parameter, and ξ_0 is the coherence distance. In both cases the gauge is to be chosen so that $\mathrm{div}\,\mathbf{j}=0$. In (1), this implies $\mathrm{div}\,\mathbf{A}=0$, and this is also true of (2) for most cases of practical interest. Pippard suggested that the kernel be taken as $J(R,T)=\exp(-R/\xi_0)$. To account for the fact that the

penetration depth, λ, of even impure specimens seems to follow the empirical law

$$\lambda(t)/\lambda(0) = (1-t^4)^{-\frac{1}{2}}, \quad (t=T/T_c). \qquad (3)$$

he also suggested that ξ_0 and Λ increase with t in a similar manner.

The theory of superconductivity of Bardeen, Cooper, and Schrieffer,[2] as modified by Mattis and Bardeen[3] to take impurity scattering into account, gives a form similar to (2), but with ξ_0 a temperature-independent parameter and $J(R,T)$ a relatively slowly varying function of temperature. The temperature dependence of the penetration depth then comes almost entirely from a variation of Λ with T. It is of interest to compare predictions based on the B.C.S. theory with experiment, particularly in view of the fact that the relative independence of coherence distance with temperature differs qualitatively from Pippard's suggestion.

[1] A. B. Pippard, Proc. Roy. Soc. (London) A216, 547 (1953).

[2] Bardeen, Cooper, and Schrieffer, Phys. Rev. 108, 1175 (1957), referred to as B.C.S.

[3] D. C. Mattis and J. Bardeen, Phys. Rev. 111, 412 (1958).