

in the polycrystalline data for the 1 weight per cent sample, but are not established in general. In the first place the single crystal data all extrapolate to the same value of C_p/T at absolute zero. Secondly the data are linear on a C_p/T vs. T^2 plot below 3°K. The single crystal data below 3°K are shown on an expanded plot in Fig. 2. A least squares calculation shows that the common intercept at 0°K is at $C_p/T = 4.44 \pm 0.03$ mJ/deg² mole and that the linearity of C_p/T vs. T^2 has an r.m.s. deviation of less than 0.6 per cent for all four samples. Thus, below 3°K the specific heats have the form $AT + B(c)T^3$, where $A = 4.44$ mJ/deg² mole and B is concentration dependent as indicated. Above 3°K the specific heats break away from the linear region rather suddenly, especially in the case of the 0.38 per cent sample, and assume the slopes and magnitudes characteristic of the polycrystalline samples.

The meaning of the $AT + B(c)T^3$ form of the specific heat is not clear at present, but the range of concentration of these samples is so broad that a process of general importance is indicated.

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References

1. ZIMMERMAN J. E., *J. Phys. Chem. Solids* **17**, 52 (1960).
2. OVERHAUSER A. W., *Phys. Rev. Letters* **3**, 414 (1959); *J. Phys. Chem. Solids* **13**, 71 (1959).
3. MARSHALL W., *Phys. Rev.* **118**, 1519 (1960).
4. WALDORF D. L., *J. Phys. Chem. Solids* **16**, 90 (1960).

Photocapacitance effects in additively colored alkali halide crystals

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KAHN and GLASS⁽¹⁾ have recently published a paper under the above title in which it appears that theoretical work of the present author is misapplied, leading to conclusions outside the scope of the theory and at variance with conclusions of similar experimental work of the author.⁽²⁾ (This paper will be referred to as I hereafter.) The main

experiment consists of measurements of the capacitance and conductance of a photoconducting crystal containing F -centers as a function of light intensity, frequency, d.c. bias, and a.c. signal amplitude. The work in I differed from that of KAHN and GLASS in that U -centered crystals were generally used, largely avoiding bleaching effects^(3,4) arising from the applied light which occur with additively colored crystals. The F -centers were produced by gamma irradiation of U -centered crystals. In addition, the earlier measurements were made by a bridge method instead of the less accurate differencing method of KAHN and GLASS. Finally, evaporated as well as silver paint contacts were used, and the effect of thin mica blocking layers was investigated as well.

The main point at issue is that KAHN and GLASS interpret their low frequency limiting capacitance as arising from electrode space charge associated with conduction-band electrons released from F -centers by light absorption, while this conclusion was found to be untenable for the results obtained in I. Space charge theory^(5,6) shows that in the case of blocking electrodes (zero conduction current), the zero-frequency or static space-charge capacitance in the limit of zero a.c. and d.c. applied potentials (practically, for potentials less than kT/e) depends on the free electron concentration in the bulk of the material, and the high-frequency limiting conductance depends on electron mobility as well. When the application of these results to experimental measurements is appropriate, both electron concentration and mobility can thus be calculated.

For practical experimental light intensities, the concentration of conduction-band electrons is very much smaller than the concentration of filled F -centers and the recombination factor^(6,7) R is very large. Under these conditions, empty F -centers (positively charged negative-ion vacancies) are mobilized by recombination, and over an appreciable applied potential range accumulation of charge can occur simultaneously at or near anode and cathode when these electrodes are blocking. Such accumulation leads to an over-all space-charge capacitance which increases essentially exponentially with applied static potential.^(6,7) No such increase was observed by KAHN and GLASS, who applied low-frequency potentials of

up to 5 V r.m.s., or by the author, who found, in fact, a slight decrease instead.⁽²⁾ For a fixed light intensity, theory⁽⁶⁾ indicates that beyond a certain applied potential, of the order of one volt in the present case, the space-charge capacitance should stop increasing and should decrease proportionally to the (applied potential)^{-m}, where *m* is one-half or less. Such decrease occurs when an exhaustion layer (here a region where all *F*-centers are ionized) starts to form at one electrode.

The dependence of static space-charge capacitance on light intensity with bimolecular recombination can be very complicated⁽⁶⁾ since it is affected by the applied potential and electrode separation. However, the static space-charge capacitance in the limit of low applied potentials should be proportional to the square or fourth root of light intensity, with the choice depending on the recombination mechanism⁽²⁾ and electrode separation.⁽⁶⁾ No light dependence at all was found in I. On the other hand, KAHN and GLASS mention that they found a fourth-root dependence, indicating bimolecular recombination, for a KBr crystal. No details or results of measurements were presented. Because of the clear dependence of photoconductance and time constant on light intensity, some parallel capacitance light dependence can be observed at any frequency above that where the final low-frequency limiting capacitance appears. This apparent change occurs even when the actual low-frequency limiting capacitance change is zero, and it is felt that KAHN and GLASS observed this effect rather than a true change. Detailed measurements presented in I failed to indicate any true static capacitance change.

The above result found by KAHN and GLASS was evidently obtained with an applied potential whose magnitude far exceeded the maximum value for which the linearized theory⁽⁵⁾ they used applies. In addition, if true fourth-root capacitance light dependence were found, it should have associated with it square-root dependence of the high-frequency limiting conductance.^(2, 8) Instead a linear dependence of conductance on light intensity was found in I, consistent with the monomolecular trapping which may be expected in a situation where there will be far more shallow traps than ionized *F*-centers.⁽²⁾ KAHN and GLASS's failure to demonstrate bimolecular recombination makes suspect their derivation of recombination

constants and electron lifetimes from measured capacitance vs. frequency curves.

Electrodes made using silver paint were termed rectifying in I, implying that conduction-band electrons could be removed relatively easily from the crystal in the forward direction of current flow but could only be brought in from the electrodes in the reverse direction with difficulty. The current-voltage relation to be expected with two such electrodes in series would be antisymmetrical in applied voltage, in good agreement with results found by KAHN and GLASS. The measurements of I indicated that the parallel capacitance (excluding the geometric contribution) of a crystal with rectifying contacts decreased at high frequencies less rapidly than the usual inverse-square power of the frequency, indicating the presence of a series capacitance dependent on frequency. The less accurate results of KAHN and GLASS show somewhat similar behavior although fitting to Debye curves is attempted. Only when the contact was made blocking in the earlier work by insertion of a thin mica sheet between the metal and the crystal was the usual frequency-independent series capacitance observed. However, the resulting over-all series capacitance was not appreciably affected by the capacitance of the mica itself, although it was quite different from that found with rectifying contacts.

The above results indicate that the character of the electrode has an important effect on the measured capacitance and that again a theory appropriate for blocking electrodes does not give a good description of the experimental results found with rectifying ones. KAHN and GLASS obtain a V^2 dependence of current on applied d.c. voltage *V* and interpret this result as a space-charge-limited current situation.^(9, 10) Results of VON HIPPEL *et al.*⁽¹¹⁾ show, however, that internal field emission is possible for applied voltages in the range applied by KAHN and GLASS. It is likely that such emission has an important effect when a.c. potentials of 5 V r.m.s. are applied, and it may account for the difference between the series capacitance associated with the region near an electrode found with rectifying and with blocking electrodes.

In an effort to explain the voltage independence of the photo-capacitance, KAHN and GLASS have presented an approximate theoretical treatment of

current flow in which the influence of positively charged ionized F -centers is omitted. This approximate treatment does indeed lead to a voltage-independent capacitance, but it turns out that when the usual space-charge-limited current result is used for the proportionality factor α introduced by KAHN and GLASS, their capacitance result simplifies to just the geometrical capacitance of the system in the absence of space charge. This capacitance is, of course, constant by definition. Further, it is inconsistent to justify the use of a capacitance result derived for blocking electrodes by means of a theory of non-zero conduction current which is applied over a range of potentials far greater than is appropriate for the original calculation.

The above considerations suggest that the conclusions of I are still valid. No true photocapacitance is measured. Instead, there is a thin region near each electrode in which there may be no F -centers (Mott barrier) or where many traps (initially probably neutral) capture electrons.^(10,12) If electrons from the bulk of the crystal cannot enter this region freely and its charge, if any, therefore changes little with applied potential, it will produce an approximately potential-and-frequency independent differential capacitance in series with the bulk conductance of the rest of the crystal. The effect of such a potential-independent capacitance in series with space-charge capacitance has been considered elsewhere.⁽⁷⁾ F -center light will increase crystal conductance and therefore cause the parallel capacitance of the system to depend on frequency except at frequencies far below the frequency corresponding to the time constant of the system. In the dark, little or no parallel capacitance will be measured at practical frequencies because the time constant will be so long. Apparently, any photo-controlled space-charge capacitance associated with the motion of free electrons in the crystal is much greater than the capacitance of the initial layers next to the electrodes and has little influence on the over-all capacitance. Measurements of the static or limiting low-frequency differential capacitance of the system as a function of temperature would be of great value in determining the cause of the potential-independent electrode capacitance.

Since the formula for low-voltage space-charge capacitance is not applicable to KAHN and GLASS'S

results, the approximate agreement of the electron mobilities they calculate with directly measured values must be a coincidence. They have failed to demonstrate the applicability of the linearized a.c. space-charge theory to their experiments, and their conclusion that their data is in striking agreement with this theory must be rejected.

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References

1. KAHN D. and GLASS A. J., *J. Phys. Chem. Solids* **17**, 210 (1961).
2. MACDONALD J. R., *J. Chem. Phys.* **23**, 275 (1955).
3. CASLER R., PRINGSHEIM P. and YUSTER P., *J. Chem. Phys.* **18**, 887 (1950).
4. HARDTKE F. C., SCOTT A. B. and WOODLEY R. E., *Phys. Rev.* **119**, 544 (1960).
5. MACDONALD J. R., *Phys. Rev.* **92**, 4 (1953).
6. MACDONALD J. R., *J. Chem. Phys.* **30**, 806 (1959).
7. MACDONALD J. R., *J. Chem. Phys.* **29**, 1346 (1958).
8. KLASSENS H. A., *J. Phys. Chem. Solids* **7**, 175 (1958).
9. MOTT N. and GURNEY R., *Electronic Processes in Ionic Crystals* (2nd Ed.) p. 172. Oxford University Press (1948).
10. RHYS-ROBERTS C. and TREDGOLD R. H., *Proc. Phys. Soc. Lond.* **76**, 497 (1960).
11. VON HIPPEL A., GROSS E. P., JELATIS J. G. and GELLER M., *Phys. Rev.* **91**, 568 (1953).
12. MOTT N. and GURNEY R., *Electronic Processes in Ionic Crystals* (2nd Ed.) p. 173. Oxford University Press (1948).

Effects of gaseous impurities on the magnetic properties of copper

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RECENT experiments on the influence of gaseous impurities on the resistance minimum and residual resistance of copper^(1,2) have shown that oxidation of 99.999 per cent copper causes a reduction in residual resistance and the disappearance of the anomalous resistance minimum. Since small concentrations of iron are known to induce a resistance minimum in copper, it was felt worthwhile to investigate the magnetic behavior of nominally pure copper upon annealing in reducing and oxidizing atmospheres.

In the Faraday method of measuring the magnetic susceptibility, a change in force due to a