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Further experiments with microwaves on the mechanisms of photographic image formation *

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Summary.

The two stages of the Mitchell theory of photographic processes, which are concerned with the trapping of the photoproduced positive holes, have been investigated in AgCl containing CuCl impurities and in AgBr containing CdBr₂ impurities. In both cases, experimental evidence is given for the operation of the mentioned stages. After the trapping of the holes, pairs of defects (interstitial silver ions and cation vacancies) are created, in positions nearest to the impurity. This happens also in the case of Cd++ impurities and gives rise to unexpected phenomena which are attributed to dielectric relaxation. The hypothesis that an association of holes and vacancies occurs is consistent with the present experiments, although no E.S.R. signal from such centres has been as far detected.

1. Evidence for the operation of the Mitchell theory in AgCl crystals containing CuCl.

It has been recently demonstrated by Electron Spin Resonance (E.S.R.) technique, that in crystals of AgCl containing traces of CuCl, the Cu⁺ ions (which occupy substitutional positions in the lattice) provide traps for the positive holes which are created by illumination [1]. The trapping of positive holes converts cuprous into cupric ions and these give an E.S.R. signal. It has to be stressed that this signal is obtained only if the crystals are frozen *very* quickly at temperatures below 130° K after irradiation: strikingly enough, at higher temperatures the signal fades very rapidly [1].

These results are in full agreement with, and have given supporting evidence for the operation in these crystals of the two important stages of the Mitchell theory of photographic processes [2, 3, 4] which are concerned with the positive holes. The first of these stages corresponds with

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the conversion of the Cu⁺ into Cu⁺⁺ ions due to the trapping of the holes. In accordance with the second stage, the fading of the E.S.R. signal was related to the passage of the silver ion from one of the twelve nearest positions around the cupric ion into an interstitial position and to its diffusion away, which occurs with a lowering of the free energy.

Nevertheless, the ultimate destination of the positive holes demanded further investigation, since the fading of the E.S.R. signal due to the cupric ions seemed to be not paralleled by the appearance of a new signal due to the same holes trapped at some different sites. We have therefore attempted a better search for such a signal. The search has been performed in various conditions, at various power levels and temperatures. The first (preliminary) results have been nevertheless negative. It has to be noted that as shown by Känzig at al. [5, 6] the E.S.R. of holes may be masked or impaired by the spin-lattice relaxation time and its temperature-dependence.

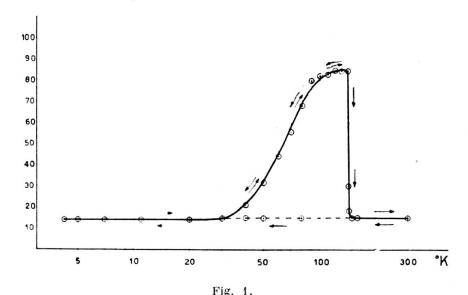
We have next investigated the possibility that the fading of the E.S.R., which occurs by raising the temperature, is due to a migration of holes as such. In this case, raising the temperature of a crystal of AgCl: Cu⁺, illuminated and rapidly cooled, from 90° K to, say, 150° K one should find a burst of electrical conductivity at the temperature at which the fading of the E.S.R. comes in. In preliminary measurements we have not found that burst and this seems to support the provisional hypothesis that if the fading of the E.S.R. is due to the diffusion of the holes away from the cuprous ions, the holes diffuse associated with centres carrying an opposite charge so that there cannot be a net charge flow.

One could then suppose that the holes might be trapped at positive ion vacancies and diffuse associated with the latter. Against this hypothesis there are reasons which suggest that the binding energy between holes and positive ion vacancies should be small [7]. Furthermore dark conductivity experiments [8] have evidenced that the bromine dissolves in crystals of Ag Br in the form of non-associated positive holes and positive ion vacancies. It seems anyway worth to note that in the quoted experiments [8] the concentration of bromine (i.e. of holes and vacancies) diffusing within the crystal was such that, for any reasonable value of the binding energy between holes and vacancies, the expected resulting association was negligible. In other words the quoted experiments of Luckey and West [8] do not seem in contradiction with the above provisional hypothesis.

2. MITCHELL THEORY AND DIELECTRIC RELAXATION IN Ag Br containing Cd++

At the advice of Prof J. W. Mitchell (who also has generously supplied, together with Dr. E. A. Braun, a large single crystal of adequate purity) we have extended the investigations on the trapping of positive holes to Ag Br crystals containing about 10^{-4} Mole of Cd Br₂. A very striking result was obtained in this case. In fact, in order to investigate the very first stage of the hole trapping process, we used here again the technique of cooling very rapidly the specimen at about 90° K following irradiation: the so treated specimen severely impaired and often prevented the electrical resonance of the microwave cavity (at the frequency of about 10^{4} Mc/sec).

The temperature-dependence of these losses is summarized in Fig. 1,



Radio Frequency (10⁴ Mc/sec) losses (arbitrary units) vs. temperature in Ag Br containing 10^{-4} mol. of Cd Br₂ following illumination at 300° K and quick cooling at 90 °K (see text).

in which the arrows evidence the irreversibility of the changes occurring at about 142° K. It has to be noted that Fig. 1 has not a strict quantitative meaning, due to the difficulty to measure or derive a quantity exactly proportional to the losses. To make clearer the nature of the latter we have performed D.C. conductivity measurements on the same samples (which were lossy at 10⁴ Mc/sec). It was again surprising to find that the D.C. conductivity of these crystals was actually of the order of

that of the best insulators and that, furthermore, no discontinuity or changes were detectable in the neighbourhoods of 140° K.

The losses cannot therefore be explained in terms of a change of the D.C. electrical conductivity. One may find one explanation along the following lines. In our crystals there will not be interstitial silver ions in thermal equilibrium; this is due to the fact that the presence of the Cd⁺⁺ ions at the mentioned concentration, introduces a concentration of cation vacancies, which is several orders of magnitude larger than the corresponding concentration in pure Ag Br crystals. If the holes are trapped at cation vacancies (this trapping is favoured by the very high concentration of the vacancies) we should have a type of V-centres [7] and in these circumstances the free energy can be lowered [7] by the formation of further pairs of lattice defects, i.e. interstitial silver ions (which are needed for the formation of photographic image) and cation vacancies.

We believe that here again the Mitchell mechanism by which one extra positive charge can release (under proper circumstances) interstitial silver ions with the formation of a neighbouring vacancy, is effective. In other words, we believe that the mentioned further pairs of lattice defects are created at sites nearest neighbours to the Cd⁺⁺ ions. In fact, if this is the case, the effect of illumination and very fast cooling (at liquid air temperature) is to freeze down a situation in which many Cd⁺⁺ ions have a nearest Ag⁺ vacancy. These complexes are in a metastable state, since the corresponding association degree is low, but they cannot dissociate since ions are immobile at that temperature. They posses an electric dipole moment, therefore they can give rise to dielectric relaxation.

An order-of-magnitude calculation concerned with the possible dielectric losses seems to be consistent with the above hypothesis. If we are close to the maximum of the Debye curve (this is not a very restrictive assumption, since this curve is about two orders of magnitude wide), we get for the jump time of the Cd⁺⁺ ions into the neighbouring vacancy $\tau = \frac{1}{\omega} \approx \frac{1}{6} \ 10^{-10} \ {\rm sec.}$

Assuming that the motion is described by the usual elementary rate equation:

$$\frac{1}{\tau} \approx 2 \nu_0 \exp \left(-\frac{W}{KT}\right)$$

where W is the activation energy for the jump and ν_0 is the «triggering» frequency of the phonons which induce the jumps, we find, for the typical

value 5 . 10^{12} cps, W ≈ 0.07 eV, which can be compared with the activation energy for the motion of interstitial silver ions in Ag Br crystals.

For the loss angle, Lidiard's theory [9] gives, at 90° K and for the above process alone

tang
$$\delta_{\rm Max} = \frac{8 \pi a^2 e^2 c}{3 \epsilon_0 \text{ KT}} \approx 10^{-2}$$

where a = half lattice constant, c = volume concentration of delects, e = charge of the electron. Therefore, the Q-value of the specimen is

$$Q\,=\frac{\epsilon_1}{\epsilon_2}=\frac{1}{tang\;\delta}\approx\,100$$

and this value, compared with the Q-value of the cavity (many thousands) reasonably accounts for the impairment or destruction of the cavity's resonance, the more so as these losses are not evenly distributed along the walls, but they can be thought of as imposing new boundary conditions.

The temperature-dependence of the losses, qualitatively depicted in Fig. 1, is also consistent with an explanation in terms of dielectric relaxation. In fact, the behaviour on the range between about 30° K and 140° K and the reversibility of the changes in that range are consistent with a reasonable temperature-dependence of the phonon population, whereas the sharpness of the dependence in the range centred at 142° K, and the irreversibility of the changes, in that range are consistent with the irreversible dissociation of the Cd⁺⁺-vacancy complexes, due to the possibility of vacancies motion. In fact, to destroy the losses it is not necessary to reach the temperature of, say, 145° K, but it is sufficient to wait at some slightly lower temperature for a duration of the order of minutes or seconds.

In conclusion, we believe that the reported experiments give supporting evidence for the operation of the mentioned stages of the Mitchell theory also in the case of Cd⁺⁺ containing Ag Br, in which the role of the impurity ions for the formation of photographic image is quite different compared with the case of the cuprous impurity ions.

REFERENCES

- 1. CICCARELLO, I. S., PALMA-VITTORELLI, M. B. PALMA, M. U. Phil. Mag. (in the press).
- 2. MITCHELL, J. W., Die Phot. Empfindlkt (Helwich, Darmstadt, 1957).
- 3. Repts. Progr. Phys. (Phys. Soc., London), 20, 433 (1957).
- 4. J. Phot. Sci., 6, 57 (1958).

- 5. Woodruff, T. O. and Kanzig, W. J. Phys. Chem. Solids, 5, 268 (1958).
- 6. COHEN, M. H., KANZIG W. and WOODRUFF, T. O. ibidem, 11, 120 (1959).
- 7. MITCHELL, J. W., private communication.
- 8. Luckey, G. W. and West, W. J. Chem. Phys., 24, 879 (1956).
- 9. LIDIARD, A. B., Rept. Conf. Defects Cryst. Solids, 283 (Phys. Soc., London, 1955).

DISCUSSION

- M. Gabillard. You mention in your communication "by illuminating and quick freezing" what time is elapsed between illumination and freezing in your experiment?
- M. Palma. This certainly is a most important point in the present experiments. I am afraid I am not able to state the maximum length of time which may be allowed between irradiation and cooling at liquid air temperatures. I may say that to get reproducible results it is necessary to cool the specimen very rapidly after irradiatation, following the experimental procedure which has been described in reference (1).
- M. Freymann. Je signale à M. Palma des travaux inédits de MM. Landucci et Meinnel sur le problème qu'il étudie.

D'autre part la brusque variation qu'il observe à 142° K est-elle due à une transition de phase ou à l'absorption dipolaire Debye ?

M. Palma. — Let me first thank you very much indeed for the kind communication of the unpublished results of M. Landucci and M. Meinnel, whom I will certainly contact.

As far as a possible "phase transition" is concerned, the only change which in our opinion occurs, and to which we attribute the sharp variation of losses at about 142° K, is the dissociation of the Cd++ — positive ion vacancy complexes. This dissociation occurs at the temperature at which vacancies become mobile, since the complexes are in a frozen-in metastable state. It has to be noted that the Cadmium ions concentration is about 10-4 Mol. The activation energy obtained from the above rate equation, as well as the angle of loss, are consistent with our interpretation.

An investigation of the frequency-dependence of the losses would certainly be a direct check of the supposed Debye-type behaviour and we hope to do that in the near future. It has to be observed that, due to the width of the Debye curve, a number of measurements at frequencies very different each other, are required.