TRAPPING AND RELEASE OF PHOTOPRODUCED HOLES IN Cu^+-DOPED AgCl CRYSTALS[*]

L. Bellomonte, M. B. Palma-Vittorelli, and M. U. Palma
Istituto di Fisica dell'Università, Palermo, Italy
and Sezione Siciliana dell'Istituto Nazionale di Fisica Nucleare, Palermo, Italy

(Received June 20, 1962)

As first pointed out theoretically by Mitchell,[1] the trapping of the positive holes liberated by illumination is a most important initial step toward the formation of the photographic image in silver halides. Crystals of AgCl doped with Cu^+ ions provide a very suitable ground for investigation of this trapping.[2-6] Electron spin resonance (ESR) experiments have proved that the Cu^+ ions provide donor levels, but they also suggested that, at room temperature, the holes are not permanently trapped at these levels.[7] The opposite evidence, nevertheless, could be drawn from optical experiments.[3]

To clarify the conflicting data, thus gaining a better understanding of this important stage of the photographic image formation, we have extended the ESR experiments to AgCl crystals containing about 10^{-4} mole of CuCl and irradiated with the 436-mμ Hg line. This technique allows the observation of a true volume effect,[3,4] while the unfiltered radiation used for the first ESR experiments[7] probably gave rise mainly to a surface effect. The results are now strikingly different. They are believed to provide, concurrently with the earlier ESR results,[7] supporting evidence for the operation of the important stages of the Mitchell theory[1] concerned with positive holes. A quantitative though oversimplified analysis, furthermore, makes possible a unitary interpretation of all the currently available experimental data on this subject.

Growth and decay curves of the ESR signal due to a photoproduced positive hole trapped at a Cu^+ ion (which thus becomes a Cu^{2+} ion), are shown in Fig. 1(a) and (b). The samples were cooled to 80°K only for the time necessary for the ESR measurements. The absorption intensity was measured by comparison with a DPPH standard.

The striking difference between the present (volume) and the earlier (mainly surface) results[7] is that the trapping of the holes at Cu^+ ion sites is now much more stable, and shows a saturation behavior similar to that shown by the optical darkening.[3,4] Nevertheless, the decay of the ESR signal due to the Cu^{2+} ions is several orders of magnitude faster than that of the optical signal.[3] The decay is slower for shorter irradiations. Re-exposure of the crystals after decay restores the ESR signal, which fades again in the same way. Furthermore the ESR signal intensity shows that even at saturation only a fraction of the Cu^+ ions present in the crystals are transformed into Cu^{2+} ions.

The experimental features may be described by the following equation (in spite of the implicit crude assumptions):

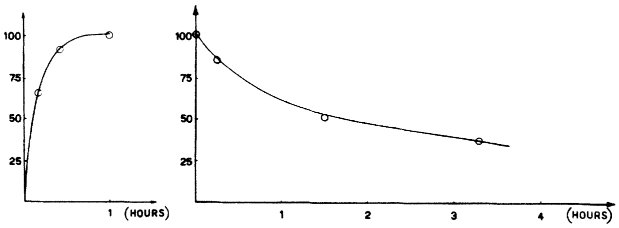
$$dn^{++}/dt = aI(N - n^{++}) - bn^{++}, \qquad (1)$$

where n^{++} = number of holes trapped at cuprous ion sites (i.e., number of Cu^{2+} ions); N = total number of copper ions (initially, they all are Cu^+ ions); I = number of photoliberated electrons per unit time (assumed to be constant); a and b are also assumed to be constants.

Integration of Eq. (1) gives

$$n^{++} = \frac{1}{1 + (b/aI)} N \left[1 - e^{-(aI + b)t} \right]. \qquad (2)$$

One then sees that all the cuprous ions will ap-



(a) (b)

FIG. 1. (a) Intensity of the Cu^{++} ESR spectrum vs irradiation time in an AgCl single crystal containing 10^{-4} mole of CuCl and irradiated at room temperature with the 436-mμ radiation. The specimen is cooled to 80°K for each ESR measurement and then the shortest possible time is allowed to elapse between warming up and further irradiation at room temperature (experiments performed at about 10 kMc/sec. (b) Typical decay of ESR intensity of the Cu^{++} spectrum in an AgCl single crystal containing 10^{-4} mole of CuCl and slightly irradiated at room temperature with 436-mμ radiation. The decay occurs at room temperature, but for each ESR measurement the crystal is cooled to 80°K. To observe a true volume effect, the sample was irradiated well be low saturation. Re-exposure of the crystal after decay fully restores the ESR signal and makes possible a reproduction of the results illustrated in (a) (experiments performed at about 10 kMc/sec).

pear to have trapped positive holes only when $aI/b \gg 1$ (i.e., at high enough irradiation intensity). For $aI/b \ll 1$ the saturation value will be

$$n^{++} = (aI/b)N, \tag{3}$$

namely, $n^{++} < N$ as we have actually found.

Let the formation of metallic silver be described by

$$dN_{\mathrm{Ag}}/dt = KI(N - n^{++}), \tag{4}$$

where N_{Ag} is the number of metallic silver atoms and K is a constant. Integration of this equation would easily show the behavior of the darkening as a function of the irradiation time and intensity.

For $t \to \infty$, Eqs. (2) and (4) yield

$$dN_{\mathrm{Ag}}/dt = KNI[b/(aI + b)], \tag{5}$$

which shows that the darkening never does saturate entirely, within the limits of validity of our assumptions. In fact, Eq. (5) yields for the rate of formation of metallic silver (after a long irradiation) a value ranging between the limits $dN_{\mathrm{Ag}}/dt = KNI$ (for low irradiation intensity) and $dN_{\mathrm{Ag}}/dt = (K/a)Nb$ (for high irradiation intensity). For a light doping, these values can be small, compared with the similar values obtainable at the start of a high-intensity irradiation, in agreement with the experimental results.[3,4]

Clearly, the assumptions contained in Eqs. (1) and (4) are very naive. In particular, a considerable darkening will affect I; in addition, a and b are not expected to be constant and, among other parameters, they will depend upon n^+ and n^{++}, respectively. More experiments are required and, in particular, an extensive search should eventually make it possible to ascertain experimentally the sites where the holes get trapped after having been released from the copper ion sites.

One possible physical picture of the above simplified analysis, as well as of the difference between the present and the earlier results,[7] may be found in the theory put forward with deep insight by Mitchell.[1]

Assuming that the earlier experiments[7] illustrated the surface effect, the holes released by the Cu^{2+} ions could then be trapped at levels associated with halide ions at surface kink sites.[1] According to Mitchell, this trapping is followed by processes which make it permanent.[1] (As a consequence of a further trapping, there could also be a partial escape of pairs of holes in the form of neutral halide molecules.[1]) This may be responsible for the fast fading of the ESR signal observed in the earlier experiments, and would provide the final step of the processes suggested in reference 7. This is also consistent with the facts that the surface darkenability is not much enhanced by the Cu^+ ions[2,4] and that the fading of the surface darkening is never as easy and complete as in the case of the volume darkening. (See references 4 and 3; this result has also been reproduced in this laboratory.)

In the present case (volume effect) hole traps which can operate as the ones provided by halide ions at surface kink sites are provided only by halide ions at jogs along edge dislocations[1]; but because of their number (and of the fact that furthermore they cannot promote even a partial escape of halide molecules), in our case they cannot control the phenomenon.[1,6] Shallow traps are provided in greater concentration by the vacancies which, according to the Mitchell mechanism, will be created together with interstitial Ag^+ ions following the trapping of holes at Cu^+ ion sites.[1,7] Therefore, if the holes released by the copper ions are trapped at silver ion vacancies, they are likely to be released again occasionally and eventually they will attack the latent image centers (and, to a lower extent, the bigger photolytic silver specks), causing their regression.[1-6] This will account for the much slower fading of the Cu^{2+}-ESR signal obtained in the present experiments, as well as for the faster and more complete fading of the volume darkening.[3,4]

This picture is consistent with the fact that the presence of the Cu^+ ions does not alter the evolution of halogen gas by irradiation with penetrating light, while it strongly enhances the volume darkenability.[4,2] It is also consistent with very preliminary optical results obtained in this laboratory which show that a new increase in the rate of darkening by re-illumination with 436-mμ radiation is found in crystals in which the ESR signal alone (rather than the darkening itself) has been allowed to fade.

The friendly assistance and help of the Director of this institute, Professor M. Santangelo, and of Dr. T. Garofano (who has supplied the crystals prepared by the Mitchell technique) are gratefully acknowledged. In the early stages of this work we had the benefit of the valuable experience of Dr. I. S. Ciccarello (now on leave of absence, at Department of Physics, University of California, Berkeley) and of much illuminating correspondence with Professor J. W. Mitchell,

who introduced us to the field.

---

*Supported by the U. S. Army European Research Office and by the Comitato Regionale Ricerche Nucleari.

[1] J. W. Mitchell, Reports on Progress in Physics (London) 20, 433 (1958), and reference to previous work by Mitchell contained therein.

[2] P. V. McD. Clark and J. W. Mitchell, J. Phot. Sci. 4, 1 (1956).

[3] F. Moser, N. R. Nail, and F. Urbach, J. Phys. Chem. Solids 9, 217 (1959).

[4] W. West and V. I. Saunders, J. Phys. Chem. 63, 45 (1959).

[5] W. West, Photochemistry in the Liquid and Solid State (John Wiley & Sons, Inc., New York, 1960), p. 128.

[6] A. S. Parasnis and J. W. Mitchell, Phil. Mag. 4, 171 (1959).

[7] I. S. Ciccarello, M. B. Palma-Vittorelli, and M. U. Palma, Phil. Mag. 5, 723 (1960).

SPECIFIC HEAT OF METALLIC PALLADIUM BETWEEN 65 AND 105°K

J. Crangle and T. F. Smith
Department of Physics, The University, Sheffield, England

(Received July 9, 1962)

Hoare and Matthews[1] found that a maximum occurs in the magnetic susceptibility of metallic palladium in the temperature region between 80 and 100°K, and following the work of Lidiard[2] there has been some speculation as to whether this maximum is associated with an antiferromagnetic Néel temperature. No confirmation of such an antiferromagnetic structure by neutron diffraction experiments has been reported, however.

It seemed profitable to examine carefully the specific heat of palladium at temperatures near the suspected Néel temperature, since this is a property which is sensitive to magnetic ordering but relatively insensitive to the physical state of the specimen. A λ-point type of anomaly is expected to occur at the Néel temperature. Previous measurements by Clusius and Schachinger[3] and later by Eichenhauer and Schäfer[4] were spaced over relatively wide intervals of temperature, and an anomaly as sharp as that reported by Beaumont, Chihara, and Morrison[5] for chromium might not have been detected. Certainly neither measurement showed any sign of an anomaly in palladium.

Our observations were made on a polycrystalline solid specimen. The palladium was chemically refined to 99.96% purity. Readings of the specific heat were taken at intervals of about $\frac{1}{2}$C° from 78 to 105°K, and at a few wider intervals below 78°K. The results are shown in Fig. 1.

It is clear that within the limits of the experimental scatter, which is 1 to $1\frac{1}{2}$%, there is no evidence of any sharp anomaly in the specific heat of palladium. A peak of the same order of size as that previously found in metallic chromium[5] and also in α-manganese,[6] both of which are antiferromagnetic, would have been easily detectable. It seems, therefore, that palladium is not an antiferromagnetic having a significant magnetic moment and a Néel temperature in the region of 90°K.

The curve from the previous measurements by Clusius and Schachinger[3] is shown in Fig. 1. It lies between $1\frac{1}{4}$ and $2\frac{1}{4}$% lower than the present measurements. This difference appears to be significant, since our apparatus has been checked by making measurements on pure iron in the same range of temperature and obtaining excellent agreement with the measurements of Kelley.[7]

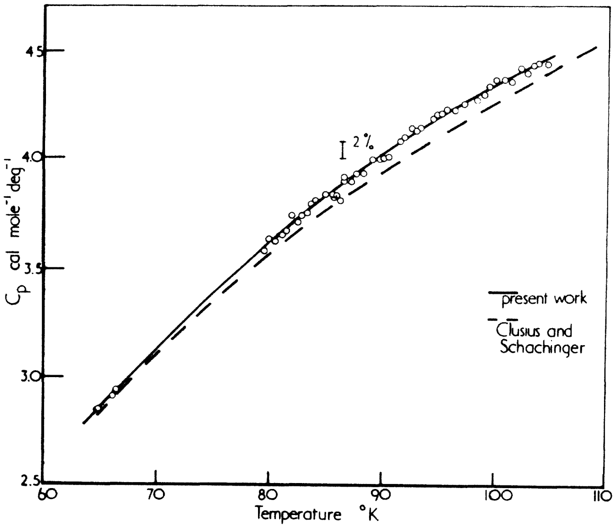


FIG. 1. The specific heat C_p of metallic palladium plotted against temperature.