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MEASUREMENTS OF THE CONDUCTIVITY
AND POLARIZABILITY
OF U AND UC AT OPTICAL FREQUENCIES

by

P. CAMAGNI, A. CINGOLANI and A. MANARA

1963



Joint Nuclear Research Center
Ispra Establishment - Italy

Materials Department
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The results are systematic enough to justify a certain comparison between the electronic structures of the two materials. However, the present data refer to polycrystalline specimens; they need to be implemented by further research on single crystals of UC and U, before definite conclusions can be reached. Such work is now in progress, using the same experimental methods.

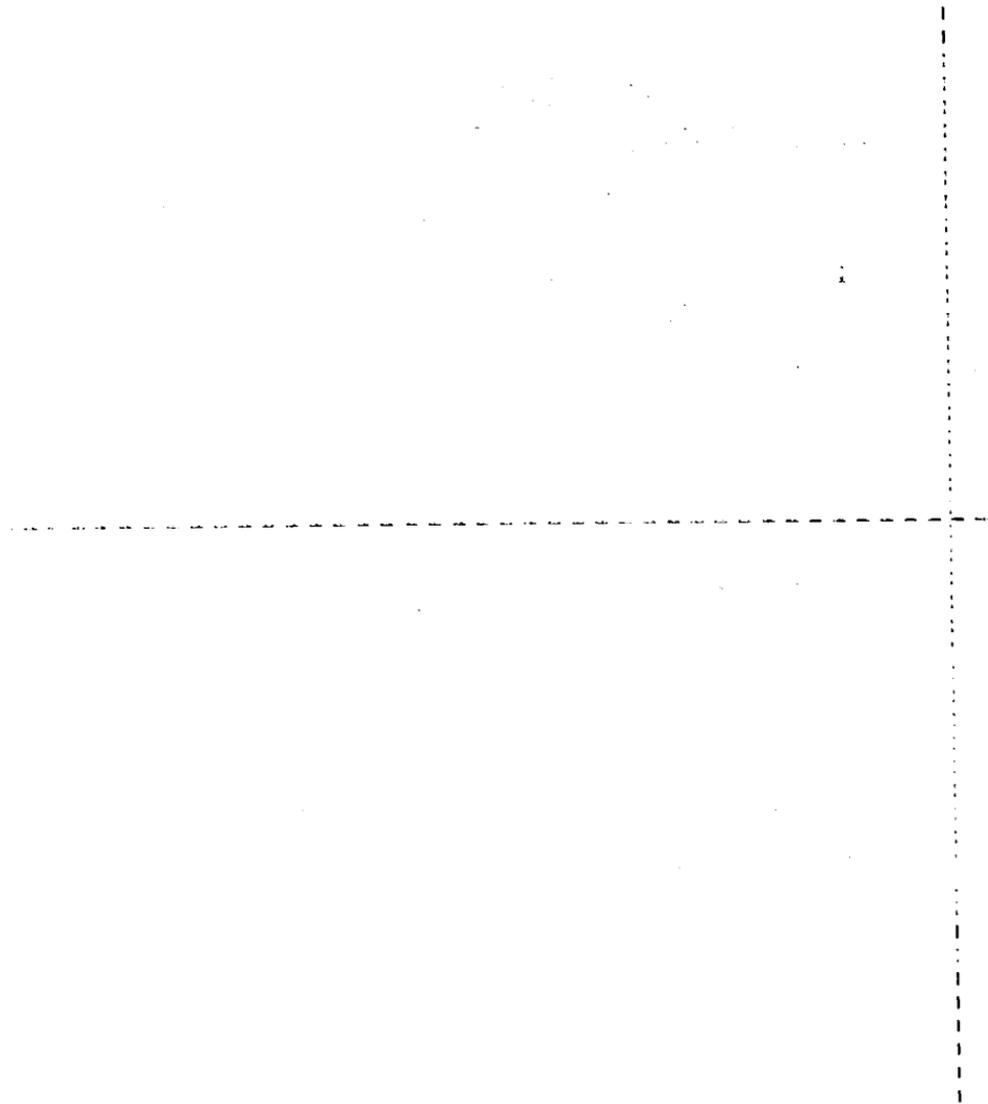
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SUMMARY

The electrical conductivity and polarizability of Uranium and Uranium Carbide have been measured at optical frequencies, by means of a technique based on the polarization of reflected light. Dispersion curves for both parameters have been determined in this way for the region of the spectrum going from $\sim 0.35 \mu$ to $\sim 2.8 \mu$.

The results are systematic enough to justify a certain comparison between the electronic structures of the two materials. However, the present data refer to polycrystalline specimens; they need to be implemented by further research on single crystals of UC and U, before definite conclusions can be reached. Such work is now in progress, using the same experimental methods.

I N T R O D U C T I O N

The optical properties of a conducting medium (metal) are expressed usually in terms of two constants: the index of refraction $n = c/v$ (where c = velocity of light in vacuum; v = phase velocity of a plane wave-front having constant amplitude) and the coefficient of extinction k , which is defined in terms of the amplitude attenuation of an electromagnetic wave when it goes through the metal.

It is known from physical optics that all developments of the basic Maxwell equations for a dielectric still hold formally for a conductor, provided use be made of a complex refraction index $N = n - ik$. It is then possible to derive a double relationship between the above said quantities n and k and the electric constants of the metal (electrical conductivity σ , dielectric constant ϵ); one finds easily the well known equations⁽¹⁾

$$n^2 - k^2 = \epsilon$$

$$nk\omega = 2\pi\sigma$$

The macroscopic constants are dependent on the angular frequency ω of the incident radiation. Their "spectral" behaviour (dispersion) reflects their relationship to the electronic structure, and has been treated by several authors on the basis of classical^(2,3) as well as quantum-mechanical theories^(1,4).

Drude treated the frequency dependence of σ and ϵ , supposing that the conducting medium contains free electrons, subjected to "viscous" damping and acted only by the electric field of the incident wave. His results are in agreement with later quantum developments, and give the following relations:

$$\sigma = \frac{n_0 e^2 \gamma}{m^* (\omega^2 + \gamma^2)} \quad (1)$$

$$\alpha = \frac{n_0 e^2}{m^* (\omega^2 + \gamma^2)} \quad (1)$$

where: γ = damping constant (reciprocal of relaxation time or collision time)

$$\alpha = \frac{\epsilon - 1}{4\pi} = \text{polarizability}$$

n_0 = number of free electrons/unit volume

m^* = mass of the electron: in the quantum mechanical case it represents the effective mass.

In addition to the effect of conduction electrons, there are usually contributions coming from the electronic transitions between normally occupied levels and empty levels of the solid. Thus for instance additional absorption takes place at certain characteristic frequencies and modifies the $\sigma(\omega)$ or $\alpha(\omega)$ curves which are predicted on the basis of free-electron theories. These problems can be dealt with quantum-mechanically^(1,4), least in principle, and formal connections can be established between the energy bands of a solid and the spectral dispersion of the optical or electric constants. The detailed theory, however, cannot be pushed very far but for the simpler metals (alkali metals).

In the specific case of Uranium Carbide, a study of the optical constants was felt to be of considerable interest for the following reasons: up to date, no direct informations on the electronic structure of this material are available; on the other hand, the complexity of the isolated U atom leads one to doubt that the problem of U-C bonding in the solid compound will ever be treated fully by

theoretical means. Some knowledge, however, might be gained by linking together the few data coming from X-ray structural studies⁽⁵⁾ with those on the d.c. electrical conductivity^(6,7). The study of the optical properties is apt to provide such link; in this respect, our research may well fit with other trends of activity of the Solid State Physics at Ispra, concerning Uranium Carbide (measurements of conductivity and thermoelectric power).

The present report accounts on a series of preliminary measurements on the optical properties of UC in the visible and near-infrared region of the spectrum. The research outlined here pointed particularly to investigate the $\sigma(\lambda)$ and $\alpha(\lambda)$ spectra, with the help of a reflection technique which is briefly described below. For obvious reasons, similar measurements were also performed on Uranium, in the hope to explore the correlations between the compound and the pure element. The data refer in both cases to polycrystalline materials.

A detailed account of the experimental methods, together with a fuller discussion of the results, will be given in a future report, when the work on single-crystal materials will be completed.

PRINCIPLE OF MEASUREMENTS

In the present work we were interested primarily to have direct measurements of σ and α . Many techniques, based on the reflection of light, are now available for the determination of these quantities (see for instance refs. 8, 9, 10). We have adopted a method which is based on the analysis of polarized light, after reflection from the material to be studied. A reflection technique is a necessary choice, since UC is known to be highly conductive, and transmission measurements would hardly be possible.

The principle of measurement is known. It was already seen that a conducting material is characterized by a complex index of refraction $N = n - ik$. By analogy with the formal treatment of non-conducting media, one may derive the refraction law $\text{sen } \theta_i = N \text{sen } \theta_r$; however, if N is complex, it follows that θ_r is also complex⁽¹¹⁾.

Let us suppose that a linearly polarized electromagnetic wave impinges on the conductor; the azimuth of polarization be given by $\text{tang } \varphi_i = \frac{A_{\perp}}{A_{\parallel}}$, where A_{\parallel} and A_{\perp} are the amplitude components of the incident light which are parallel or perpendicular to the incidence plane. Formally, there is a well known link between these components and the corresponding components R_{\parallel} and R_{\perp} of the reflected light; this is provided by Fresnel's relations:

$$R_{\parallel} = \frac{\text{tg } (\theta_i - \theta_r)}{\text{tg } (\theta_i + \theta_r)} A_{\parallel}$$

$$R_{\perp} = \frac{\text{sen } (\theta_i - \theta_r)}{\text{sen } (\theta_i + \theta_r)} A_{\perp}$$

The azimuth φ_r of polarization for the reflected light will be given by

$$\text{tg } \varphi_r = \frac{R_{\perp}}{R_{\parallel}} = \frac{\cos (\theta_i + \theta_r)}{\cos (\theta_i - \theta_r)} \text{tg } \varphi_i \quad (2)$$

and will be complex (in general), being θ_r a complex quantity. In other words, there simply is no linear polarization after reflection: a characteristic phase change Δ takes place between the two components (formerly in phase with each other) - and consequently the reflected light is elliptically polarized. The relationship 2) can be written also in the form

$$\frac{R_{\perp}}{R_{\parallel}} = \rho e^{-i\Delta} \operatorname{tg} \varphi_i \quad \text{where} \quad \left| \frac{R_{\perp}}{R_{\parallel}} \right| = \rho \operatorname{tg} \varphi_i$$

It can be seen clearly that by making two independent measurements i) on the absolute ratio of the reflected components R_{\perp} , R_{\parallel} , and ii) on the orientation of the major axis of the ellipse, we determine the two elements ρ and Δ ; these in turn are connected to θ_r , therefore to $n - ik$ (see 11): thus the real part n and the imaginary part k of the complex index may be evaluated. Actually the equations giving n and k in terms of the experimental quantities are often complicated, depending on the method at hand^(8,11).

EXPERIMENTAL METHOD

In order to analyze the state of polarized light after reflection from a specular surface of UC, we have set up^a technique which is based on the method of Beattie⁽¹²⁾.

The experimental apparatus is described schematically in figure 1). A beam of monochromatic light goes through a first polarizing nicol, whose azimuth of vibration is $\pi/4$ with respect to the plane of incidence (plane of the figure). After reflection from the sample, the radiation passes through a second nicol, which is used as the analyzer; finally the light goes to a detector. The analyzing nicol is rotated on succession into four distinct vibrational azimuths, giving rise to four different levels in the intensity of the transmitted light:

- I_1 (analyzer \perp to the plane of incidence)
- I_2 (analyzer \parallel to the plane of incidence)
- I_3 (analyzer at $\pi/4$ to the plane of incidence)
- I_4 (analyzer at $-\pi/4$ to the plane of incidence).

The above defined intensities are measured by an infrared-sensitive cell or by a phototube according to the region of the spectrum to be explored. The signals are fed into a frequency-analysing voltmeter; this is tunable at the frequency of modulation of the light, which is intercepted at a rate of ~ 240 cycles/sec. by a rotating sector set in front of the primary source. Signal modulation is adopted, as usual, in order to minimize problems of drift and dark-current, typical of d.c. detection.

In the method of Beattie the parameters ρ and Δ are connected to the above said intensities by the following relationships:

$$\rho = \sqrt{I_2/I_1}$$

$$\cos \Delta = \frac{1}{2} \left(\rho + \frac{1}{\rho} \right) \frac{I_3 - I_4}{I_3 + I_4}$$

These quantities, together with the measured angle of incidence θ , allow us to evaluate directly \underline{nk} and $n^2 - k^2$ (i.e. conductivity and polarizability), when use is made of the known equations given in the theories of physical optics^(8,11). In particular, working at a special angle of incidence $\bar{\theta}$, which is called the principal angle, and is characteristic of the material, one has $\Delta = \pi/2$ and formulae reduce to:

$$n^2 - k^2 = \text{sen}^2 \bar{\theta} \tan^2 \bar{\theta} \frac{(1 - \rho^2)^2 - 4\rho^2}{(1 + \rho^2)^2} + \text{sen}^2 \bar{\theta}$$

$$\underline{nk} = \text{sen}^2 \bar{\theta} \tan^2 \bar{\theta} \frac{2\rho(1 - \rho^2)}{(1 + \rho^2)^2}$$

The accuracy in the determination of the optical constants is essentially conditioned by the measure of ρ , i.e. of the ratio I_2/I_1 . This is especially true, when one operates in such conditions that $I_3 - I_4 \approx 0$ (in this case Δ is equal to $\pi/2$, and the angle $\bar{\theta}$ is, as we said, the

principal angle of incidence: it could be seen, following Beattie, that these conditions correspond to minimizing the systematic errors connected with angular measurements).

The light source was a standard tungsten-filament lamp for spectrophotometric work in the visible and near-infrared region.

The monochromator was a Hilger & Watts, with interchangeable prisms; it was used with a quartz or a glass prism for the range 0.35μ — 2.8μ .

The samples of U and UC were in the form of polycrystalline discs. The reflecting face was polished down to optical planarity with the use of emery papers and diamond paste; the surface was then cleaned of all dirt or oxidized layers by means of a rinse in a suitable ultrasonic bath^(°).

The samples were mounted onto a goniometer, especially designed and equipped for measuring incidence and reflection angles.

The nicols were in Calcite, with a polarization efficiency well over 99%; they are sufficiently transparent up to about 2.9μ .

The infrared detector was a PbS photoconductive cell of Eastman Kodak, Type Ektron N-2. The photomultiplier was the E.M.I. type 6255 for visible and u.v.

The tunable voltmeter is a Bruel & Kjaer type 2105 (45 Hz to 12.000 Hz).

(°) We acknowledge gratefully the assistance received from the Section of Metallography (Metallurgy, C.C.R.) in the preparation of our samples.

RESULTS

Systematic calibrations have been performed in the first place, by measuring the $\sigma(\lambda)$ characteristics of monocrystalline Cu. It can be seen in fig. 2) that our values of σ are in consistent agreement with those reported in the literature: account must be taken of the large dispersion of the few existing data, admittedly due to the difficulty of preparation of suitable optical surfaces.

For U and UC, reflection measurements were performed in the range 3000 Å to 28.000 Å: the data for $\sigma(\lambda)$ are reported in fig. 3) for Uranium and in fig. 4) for UC. The data for the polarizability are reported in Table I, limited to the range between 1.3 μ and 2.8 μ .

In both curves of $\sigma(\lambda)$ the extreme branch towards the larger wavelengths appears to be due to free-electrons; this could be checked by us on the basis of the expectation from Drude's theory. As a matter of fact, if eqs. 1) are valid, it follows that σ must be a linear function of α , precisely $\sigma = \gamma\alpha$ at all wavelengths. The diagrams of σ vs. $(1-\epsilon)$ in figs. 5) and 6) show that this indeed is the case for U (above 1.3 μ) and for UC (above 2 μ). The slope of the straight lines gives obviously the value of $\gamma/4\pi$ (damping constant, reciprocal of the relaxation time): one finds from the present data that $\gamma_U = 5.3 \times 10^{14}$ and $\gamma_{UC} = 18 \times 10^{14}$. Thus the relaxation time appears to be sensibly smaller in the compound, as one might reasonably expect.

At smaller wavelengths (below 1.3 μ and 2 μ respectively for U and UC) the curves of $\sigma(\lambda)$ show a series of structures: these are probably due to electronic transitions between normally occupied levels and empty levels characteristic of the band scheme of the two materials. One may observe that there is a significant correspondence between the two structures: more precisely, the peaks of UC resemble those of Uranium, with a general shift towards smaller energies.

Such similarity in the optical behaviour might suggest that the electronic levels in UC are not drastically altered with respect to Uranium: thus the effect of U-C bonding would be merely to alter the electronic density so as to bring the highest occupied levels nearer to empty levels of the next band. However, the significance of these remarks must be limited for the time being, owing to the fact that the present data are preliminary, obtained as they are from polycrystalline specimens. (For instance, the data for $(1-\epsilon)$ were less clear than those for conductivity in the region where structures appear). Heterogeneities connected with the microcrystalline structure of the U and UC available to us might have affected our measurements, especially those of the dielectric constant.

Work has already begun on single-crystal UC, and will be extended as soon as possible to single crystal Uranium. In connection with this more critical research, the apparatus is also being improved in order to take our measurements further out in the infrared region, and thus explore more systematically the range where free-electron contribution predominates.

TABLE I

Measured values of $(1 - \epsilon)$, i.e. $4\pi\alpha$

| λ (microns) | U | UC |
|---------------------|------|------|
| 1.3 | 5.4 | 2.6 |
| 1.4 | 6.6 | 2.4 |
| 1.5 | 8.1 | 2.0 |
| 1.6 | 9.2 | 3.1 |
| 1.7 | 13.6 | 3.8 |
| 1.8 | 14.5 | 5.0 |
| 1.9 | 17.6 | 6.3 |
| 2.0 | 18.9 | 7.4 |
| 2.1 | 21.2 | 10.0 |
| 2.2 | 24.6 | 11.0 |
| 2.3 | 29.4 | 12.5 |
| 2.4 | 30.0 | 13.0 |
| 2.5 | 31.6 | 15.0 |
| 2.6 | 33.4 | 17.0 |
| 2.7 | 34.6 | 19.0 |

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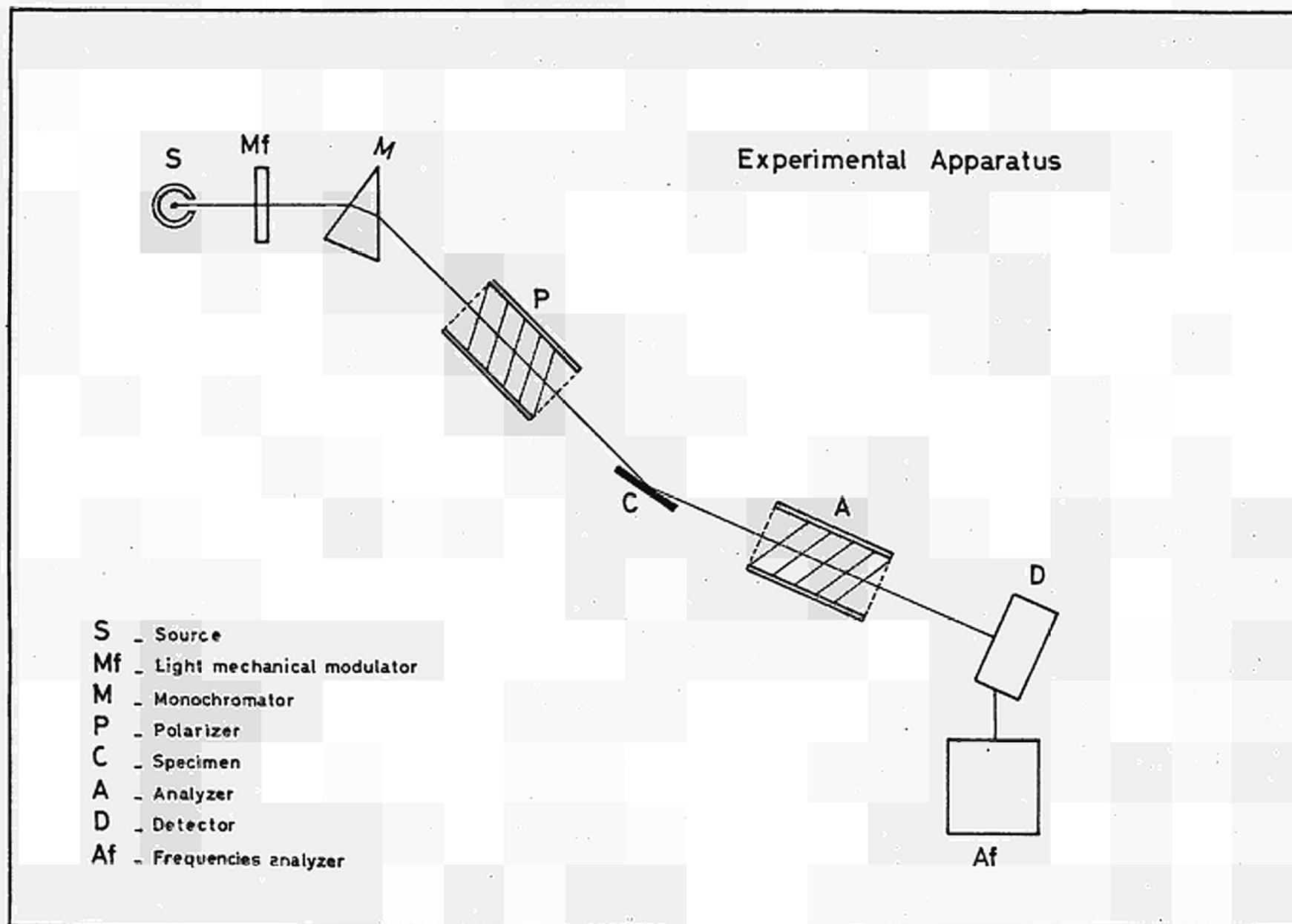


Fig. 1 Block diagram of experimental apparatus

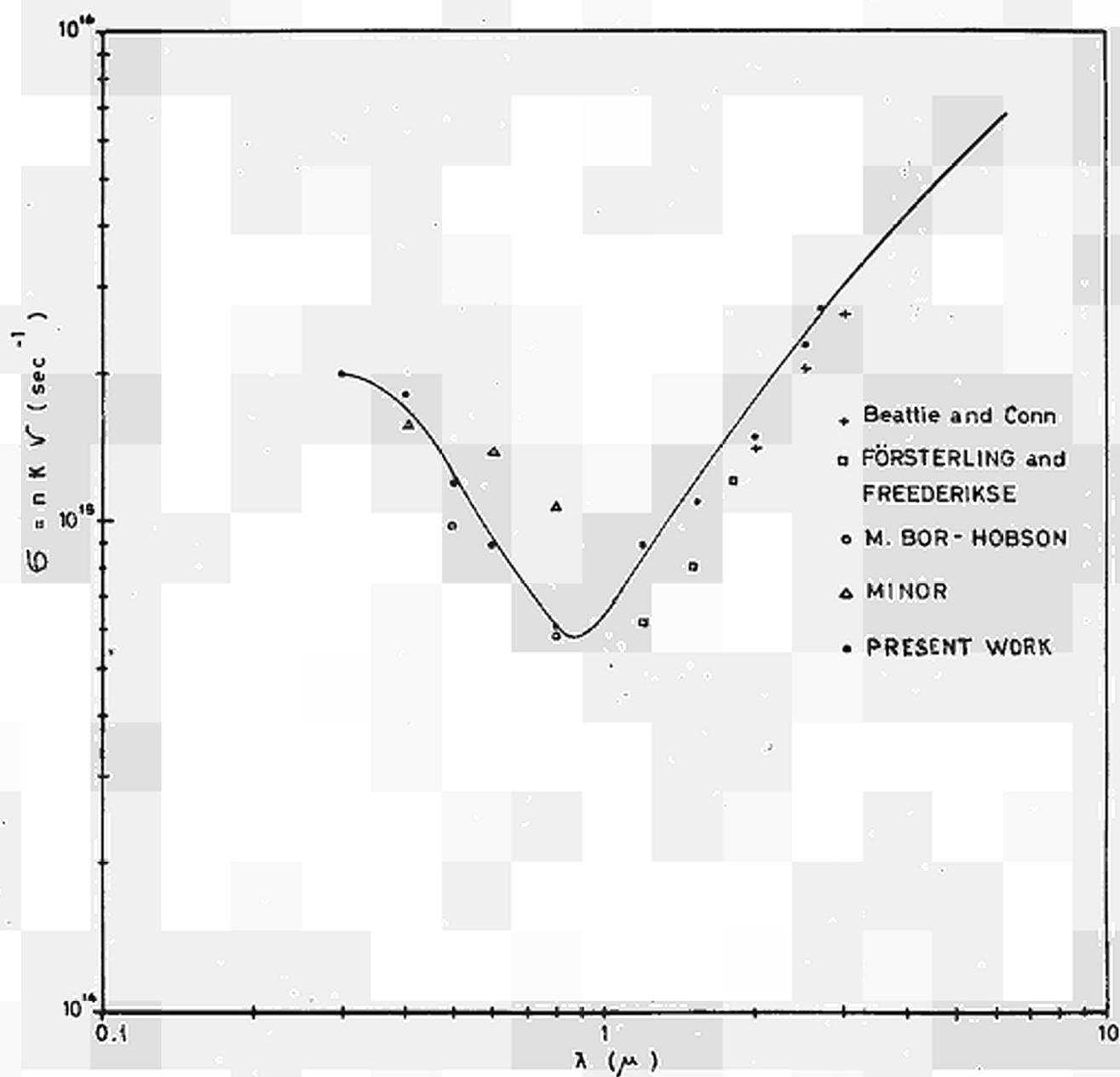


Fig. 2 Dispersion of conductivity, σ vs. λ , in monocrystalline Cu.

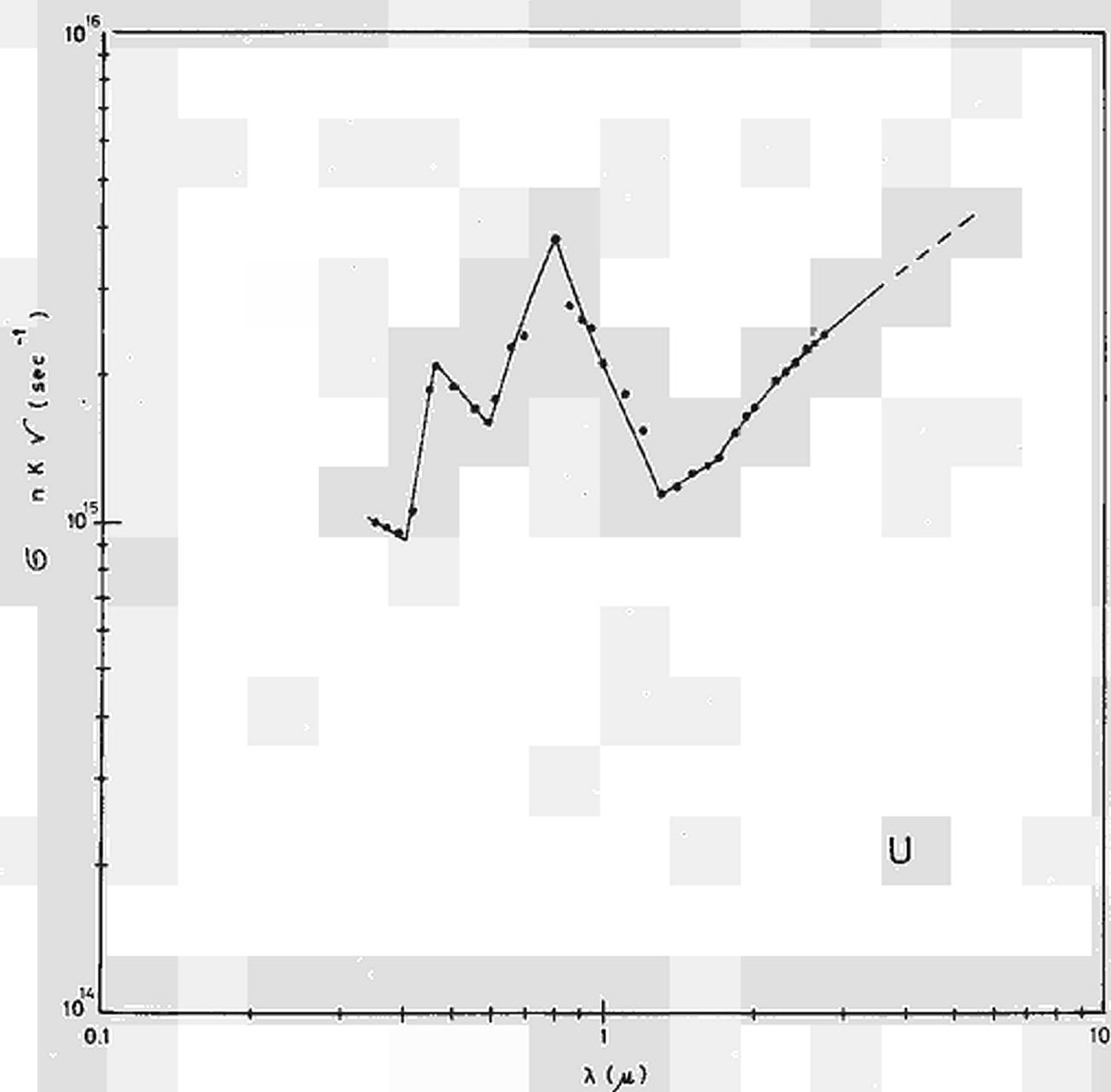


Fig. 3 Dispersion of conductivity, σ vs. λ , in polycrystalline Uranium

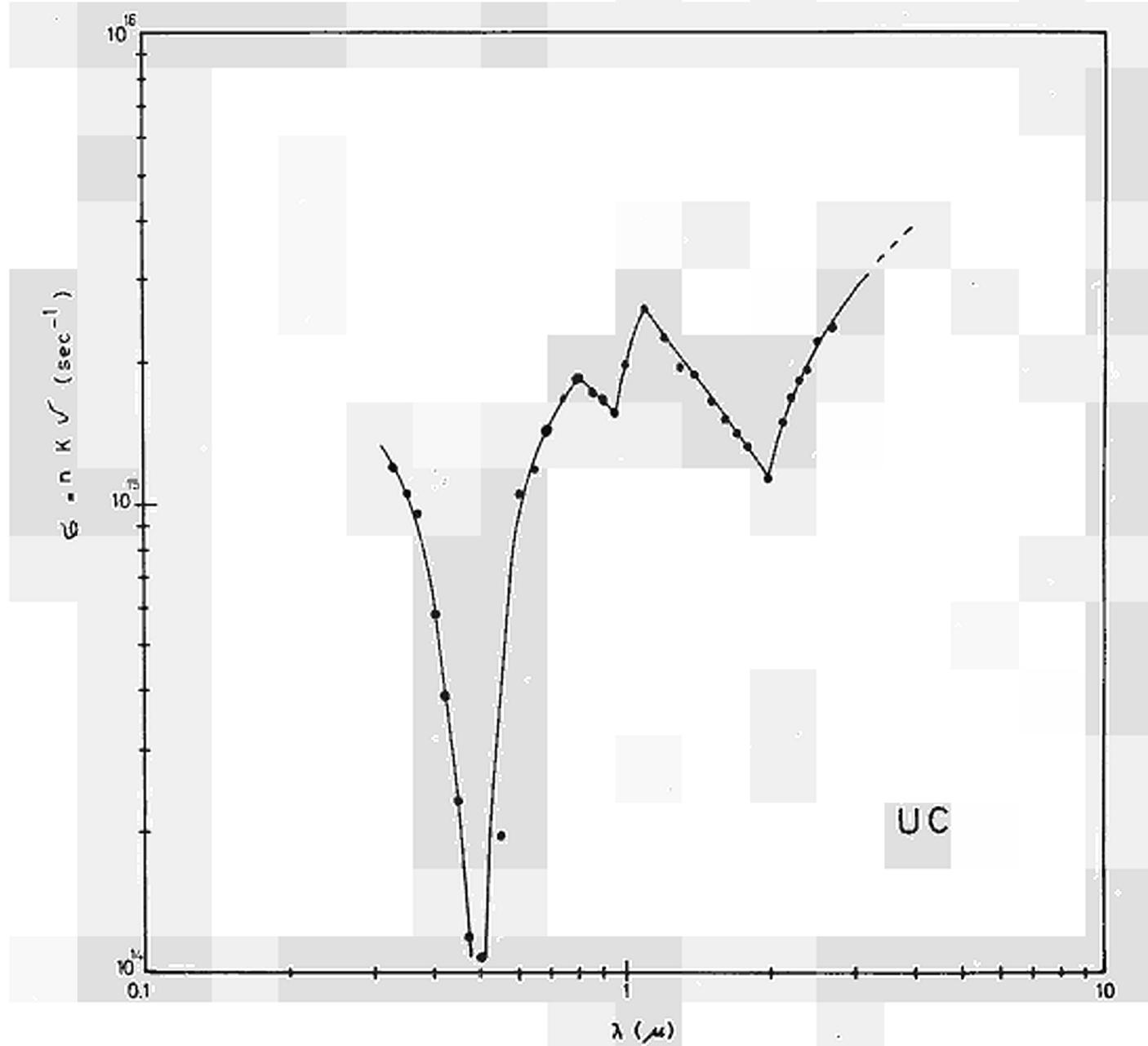


Fig. 4 Dispersion of conductivity, σ vs. λ , in polycrystalline Uranium Carbide

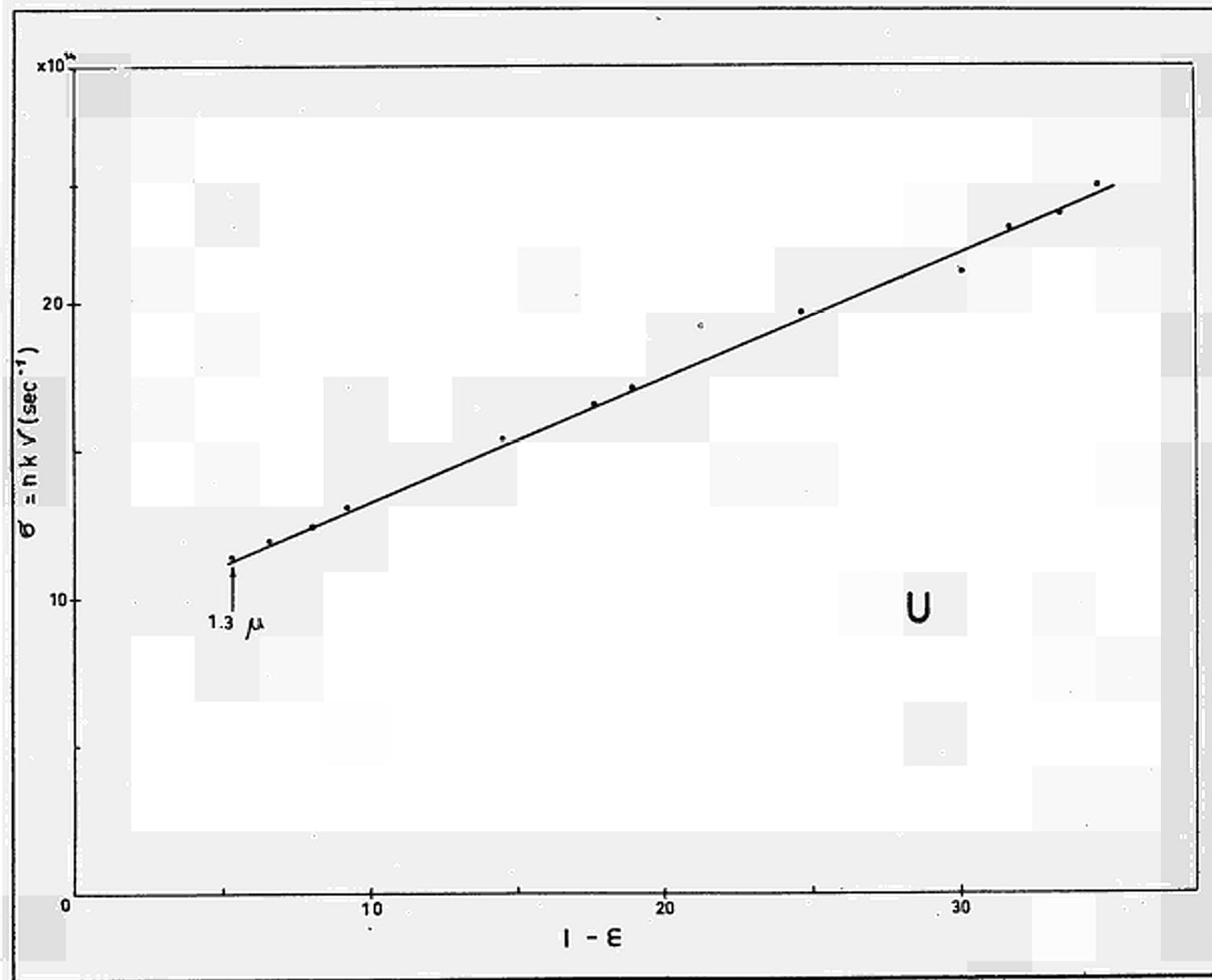


Fig. 5 Plot of conductivity σ versus polarizability $(1-\epsilon)$ for U.

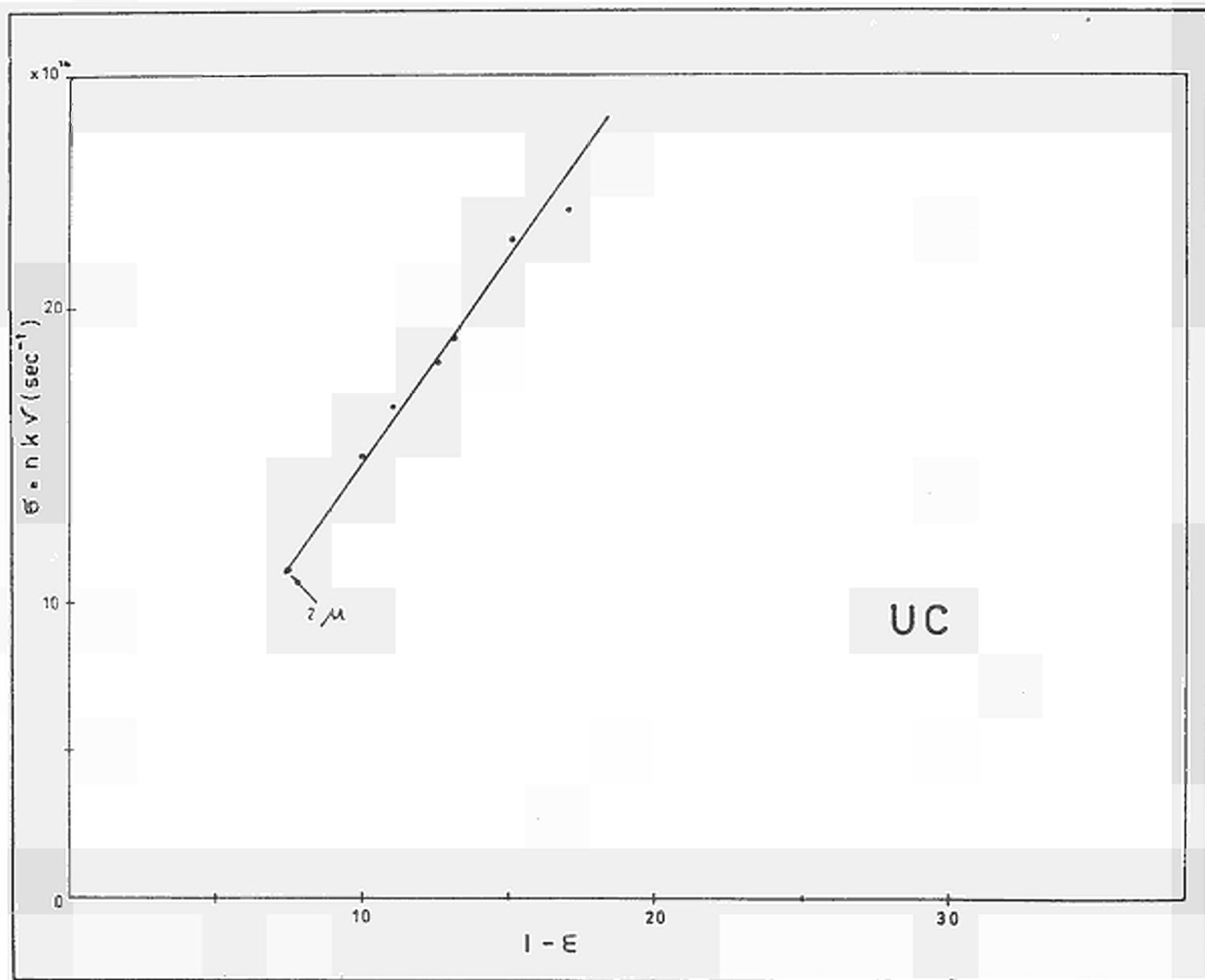


Fig. 6 Plot of conductivity δ versus polarizability $(1 - \epsilon)$ for UC.

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