KERNFORSCHUNGSZENTRUM

KARLSRUHE

April 1973 KFK 1838

Institut für Material- und Festkörperforschung
Projekt Schneller Brüter
Projekt Nukleare Sicherheit

The Porosity Dependence of the Thermal Conductivity for Nuclear Fuels

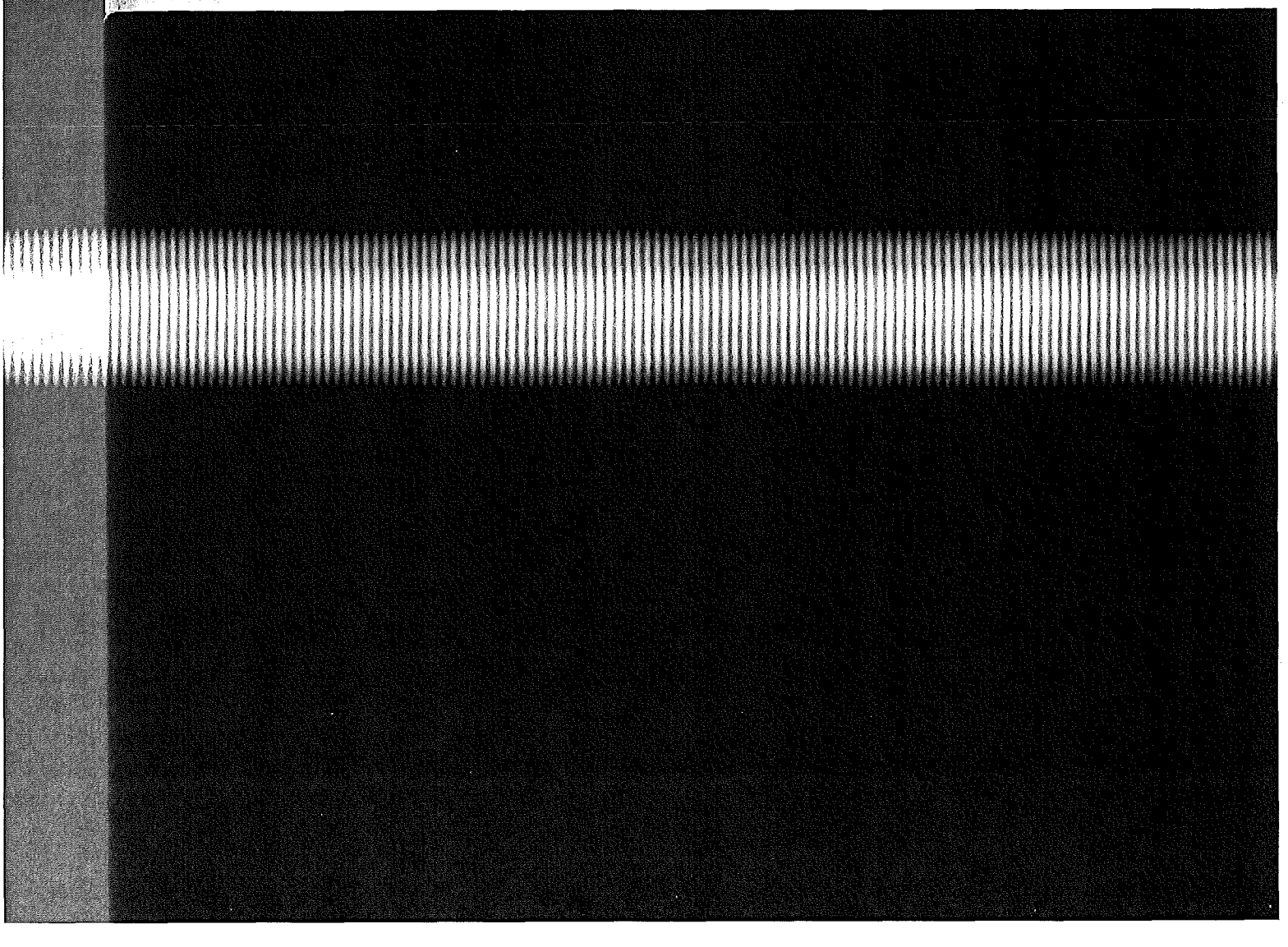
G. Ondracek, B. Schulz

GESELLSCHAFT FÜR KERNFORSCHUNG M. B. H.

KARLSRUHE

Erratum

In fig. 1 and fig. 2 the slope of the theoretical curve between o and 1o % porosity is convex with respect to the top of the figures caused by an error in the drawing. It should be slightly concave, which results in an even better agreement with the experimental values.



JOURNAL OF NUCLEAR MATERIALS 46 (1973) 253–258. © NORTH-HOLLAND PUBLISHING CO., AMSTERDAM

THE POROSITY DEPENDENCE OF THE THERMAL CONDUCTIVITY FOR NUCLEAR FUELS

G. ONDRACEK and B. SCHULZ

Institut für Material- und Festkörperforschung, Kernforschungszentrum Karlsruhe, Germany

Received 24 October 1972

A critical consideration is given to equations used in several papers to describe the dependence of thermal conductivity on porosity. It is shown that the only method of derivation justified physically is that starting from the general field equation. In this way following the methods of Maxwell, Bruggeman and Niesel two equations have been derived, the calculated values of which agree closely with the experimental values of the thermal conductivity for porous UO_2 and UN. In these equations two clearly defined stereometric factors appear, which take into account the effect of the shape and the orientation of the pores on the thermal conductivity. These factors can be calculated by using stereometric data measured in the microstructural sections. The reason one obtains two equations lies in the fact that two types of porosity occur: closed isolated as well as interconnected porosity. The equations and their means of derivation are explained.

Une étude critique des équations utilisées dans plusieurs articles pour décrire les relations entre conductivité thermique et porosité des combustibles nucléaires est présentée. On montre que la seule méthode de dérivation justifiée physiquement est celle basée sur l'équation générale du champ. De cette manière, en s'inspirant des méthodes de Maxwell, Bruggeman et Niesel, deux équations en ont été déduites et les valeurs calculées à partir de celles-ci s'accordent de près avec les valeurs expérimentales de la conductivité thermique dans le cas des combustibles poreux UO_2 et UN. Dans ces équations apparaissent deux facteurs clairement définis qui prennent en compte l'effet de la forme et de l'orientation des pores sur la conductivité thermique. Ces facteurs peuvent être calculés en utilisant les données stéréométriques mesurées sur les coupes de la microstructure. La raison pour laquelle on obtient deux équations repose sur le fait que deux types de porosité se produisent: des pores fermés aussi bien que des pores interconnectés. Les équations et la façon de les dériver sont explicités.

Die in verschiedenen Arbeiten verwendeten Gleichungen zur Beschreibung der Abhängigkeit der Wärmeleitfähigkeit von der Porosität werden kritisch behandelt. Es wird gezeigt, dass der physikalisch begründete Weg der Ableitung nur derjenige sein kann, der von der allgemeinen Feldgleichung ausgeht. Auf diesem Wege lassen sich mit Ansätzen von Maxwell, Bruggeman und Niesel zwei Gleichungen ableiten, die die experimentellen Werte für poröses Urandioxid und poröses Uranmononitrid richtig beschreiben. Sie enthalten physikalisch klar definierte Stereometriefaktoren, die den Einfluss der Porenform und -orientierung auf die Leitfähigkeit wiedergeben. Diese Stereometriefaktoren sind aus Messungen am Gefüge rechnerisch bestimmbar. Zwei Gleichungen ergeben sich deshalb, weil der Einfluss geschlossener Poren anders ist als derjenige offener Poren. Die Gleichungen und der Weg ihrer Ableitung werden erläutert.

1. Theoretical background

During the last two years there have been several contributions in this journal considering how the thermal conductivity of UO_2, $(UPu)O_2$, UN and $(UTh)O_2$ depends on porosity [1–6]. In some of these publications attempts were made to compare the experimental values with those theoretically calculated. The starting point for theoretically conceiving the relationship between the thermal conductivity (k) and the porosity (P) is Maxwell's equation [7]. Frequently this equation is also attributed to Eucken [2, 4–6, 10], owing to an erroneous quotation by Kingery [9]. Eucken himself did not derive this equation but quoted Maxwell and used his equation for calculating the thermal conductivity of binary phase mixtures. For the case of closed porosity formed by isolated spherical pores of low

concentration, which do not conduct any heat, the Maxwell equation is

$$k = k_0 \frac{1-P}{1+0.5P}, \tag{1}$$

where k_0 is the thermal conductivity of the nonporous material.

Maxwell derived his equation by considering a homogeneous field in a single-phase dense material, which is changed if parts of the material are replaced by spherical particles of a second phase. The resulting field is formed by the interference of the original field and the stray field, caused by the inclusions. In the case of thermal conductivity a temperature field results which governs the thermal conductivity of the two-phase material. Assuming the limiting case that the thermal conductivity of the second phase becomes zero, eq. (1) follows and is valid for porous materials.

To avoid the superposition of stray fields caused by different pores, the pores should be separated by a certain distance. This is the reason why eq. (1) is only valid for low porosities. In addition to the total amount of pores, their distance is also dependent on their size. This follows quantitatively from the equation for the mean free distance ($\bar{\lambda}$) derived by Fullman [8]:

$$\bar{\lambda} = \bar{L} \frac{1-P}{P}. \tag{2}$$

In the equation the mean intercept length ($\bar{L}$) has been taken as a measure of the pore size. At a given porosity the mean free distance between the pores increases with their size. Hence eq. (1) can be used up to a higher porosity for larger pores than for smaller ones. Therefore it is not sufficient to relate the limit of validity of eq. (1) only to the amount of porosity.

In order to overcome the restriction to spherical pore shape several authors modified Maxwell's equation by inserting a so-called "geometrical factor" [4, 13–15]. The modified equation is of the type

$$k = k_0 \frac{1-P}{1+\beta P}, \tag{3}$$

where β is the geometrical factor. Assuming an ellipsoidal shape of the pores, both Fricke and Marino determined the geometrical factor as a function of the axial ratio of the ellipsoid as well as of the conductivities of the pores and of the matrix material [4, 15]. However, Ohm's law was used in the mathematical treatment by Fricke and this may lead to doubtful results. The reason for this statement is most clearly demonstrated by considering the equation of Kämpf and Karsten, which is totally based on Ohm's law [10]. A correct mathematical procedure following the method of Kämpf and Karsten would lead to two different equations [16]:

$$k = k_0(1-P^{\frac{2}{3}}), \tag{4}$$

$$k = k_0 \frac{1-P^{\frac{2}{3}}}{1-P^{\frac{2}{3}}+P}. \tag{5}$$

This result implies that the same porous material under given conditions could have two different conductivities. Powers had already pointed out this contradiction [27]. The reason lies in the fact that Ohm's law is an integrated form of the general field equation, restricted to special presuppositions not fulfilled in the present problem [12, 16]. Therefore the use by Marino and Kikuchi et al. of Fricke's equation together with eq. (3), in order to correct the thermal conductivity of nuclear fuels for pores is questionable. In addition the "geometrical factor" in eq. (3) is not only dependent on stereometric quantities: it can also depend on the density as well as on the temperature of the measured specimen [3, 4, 6]. Consequently β has to be determined empirically or semi-empirically. For this reason these geometrical factors are useless if the physical understanding of the porosity dependence of thermal conductivity is desired. Consequently it is only worth

considering those ways of derivation which use the general field equation as a basis, as Maxwell did.

Bruggeman followed the physically correct method of Maxwell with the aim of overcoming the restriction of eq. (1) to small pore concentrations. For this purpose he differentiated eq. (1) with respect to the porosity (P) to obtain the variation of the thermal conductivity for small increases in porosity. The integration between a conductivity zero – for "total" porosity – and the conductivity for the dense material leads to an equation without a restriction to low pore concentration [16–18, 20]. However, this equation is only valid for isolated closed pores as stated by Maxwell. To obtain a corresponding equation valid for open interconnected porosity another "thought-experiment" is necessary; this too was proposed by Bruggeman [16–18, 20]. Starting with a material consisting of interconnected pores in a bulk body, one can use Maxwell's equation if only a small amount of porosity is added. In the next step the concentration of the solid phase is increased such that the original conductivity is obtained. Again eq. (1) can be used to calculate the resulting thermal conductivity. By repeating this procedure until both phases, the pores and the solid phase achieved interconnected structure at the desired concentration, Bruggeman got a second equation valid for interconnected and open porosity without any restriction on the concentration range of the pores.

Further progress was made by Niesel [19]. He used the two equations, valid for isolated closed pores and interconnected porosity, assuming an ellipsoidal shape of the pores. His mathematical treatment led to two equations free of the restriction to spherical pores. The advantage of ellipsoidal pores as an approach to the real pore shape is the possibility of varying the axial ratios of the ellipsoids in an unrestricted range. By doing this, many irregular shapes can be approximated by ellipsoids, having the same volume and similar mean size ($\bar{L}$). Leaving the assumption of spherical pores Niesel had to take into account that another factor exists besides the shape: the orientation. Obviously the "orientation" of spheres is always "statistical". As a consequence the effect of the stray field mentioned before is now governed by two stereometric parameters: the orientation factor ($\cos^2\alpha$) and the form factor (F). Both factors appear in Niesel's equations related to two phase materials [16, 20]. From these equations, which are implicit, simpler forms can be derived for the case of nonconducting pores [20]:

$$k = k_0\,(1-P)\,\frac{\cos^2\alpha_p}{2F_p} - \frac{1-\cos^2\alpha_p}{F_p-1}, \qquad (6)$$

$$(1-P)\,(k_0-k) \times \left[\frac{1-\cos^2\alpha_0}{k(1-F_0)+k_0F_0} + \frac{\cos^2\alpha_p}{k_0(1-2F_0)+2kF_0}\right] - P\left[\frac{1-\cos^2\alpha_p}{1-F_p} + \frac{\cos^2\alpha_p}{2F_p}\right] = 0; \qquad (7)$$

eq. (6) is valid for isolated closed pores, eq. (7) for interconnected porosity. The indices are related to the matrix material (0) and the pores (p). The stereometric factors concerning the shape and the orientation can be calculated generally and determined for a specific material by measuring microstructural quantities in its plane of polish [20–24]. The limiting cases of the rotational ellipsoid are the disc and the cylinder of infinitesimal thickness. In table 1 the stereometric factors are given for these cases as well as for a sphere. Also given are three sets of orientation factors related to the statistical orientation and to the orientation of the rotational axis parallel or perpendicular to the direction of the field.

More detailed information is given in the literature [16, 20]. The stereometric factors used here are independent of temperature and their physical sense is clear. The shape factor stands for that ellipsoid which is the best approach to the average of the real pores. The orientation factor is determined by the angles (α) formed by the rotation axes of the ellipsoidal pores

TABLE 1
Values of the stereometric factors for special cases

Geometry	Shape factor (F)	Orientation	Orientation factor ($\cos^2 \alpha$)
Infinite thin disc	$F \to 0$	perpendicular to the field	0
Sphere	0.33	statistical	0.33
Infinite thin cylinder	$F \to 0.5$	parallel to the field	1

and the field direction. In sect. 2 an attempt will be made to compare experimental results taken from the literature with the theoretical values calculated by the equations given above.

2. Comparison between theoretical and experimental results

The literature data used in this section are taken from papers which at least gave a clue about the stereometric microstructure of the specimens measured. In fig. 1 the measured thermal conductivities of UO_2 and $(UPu)O_2$ are normalized by dividing them by the measured value of the nonporous material at the corresponding temperature. The margin of error, given in fig. 1 for each porosity, is caused by the fact that the values measured at different temperatures differ statistically. According to

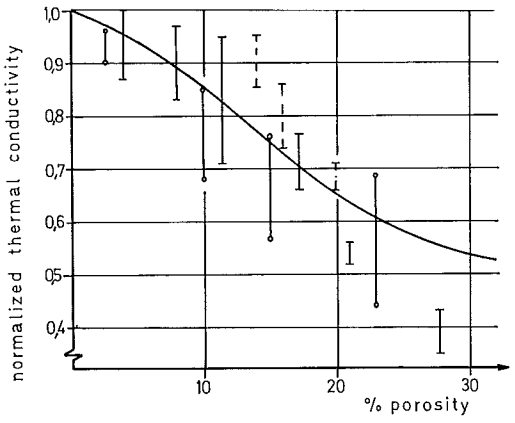


Fig. 1. The dependence of normalized thermal conductivity on porosity. Experimental values: I: UO_2 after Craeynest and Stora, T: $(U_{0.8}Pu_{0.2})O_2$ after Craeynest and Stora, ⟆: UO_2 after Müller, —: theoretical curve.

eqs. (6) and (7) the normalized thermal conductivities as functions of porosity do not vary with temperature, but only with the shape and orientation of the pores. Fig. 1 also contains values for the thermal conductivity of UO_2 which have been taken from normalized average values in the literature [26].

The information given in the literature about the specimens microstructure allows the assumption of spherical porosity for calculating a theoretical curve. It was also possible to assess the ranges for closed ($P<12\%$) and for interconnected porosity by analysing microstructural photographs given in the papers. Therefore the first part ($P<12\%$) of the curve in fig. 1 is calculated using eq. (6), ($F_p=0.33$; $\cos^2\alpha_p=0.33$) whilst eq. (7) was used for the second part. The interconnected porosity was thought to be built up by cylindrical pores ($F_p=0.5$; $\cos^2\alpha_p=0.33$) and the dense material was thought to be constructed by dense cylindrical particles of that phase ($F_0=0.5$; $\cos^2\alpha_0=0.33$). The special reason for this assumption is explained elsewhere [30]. A detailed consideration of eq. (7) shows that the influence of the shape factor (F) on the thermal conductivity in a certain region ($\frac{1}{3}\leqslant F\leqslant\frac{1}{2}$) is small in the case of interconnected phases [28]. Furthermore, there is a certain lack of accuracy in the determination of the stereometric factors in such a case [20].

Thus the formal assumption about cylindrical elementary parts in the porous materials considered here is acceptable. As can be seen in fig. 1 some experimental values do not touch the theoretical curve, especially in the range corresponding to interconnected porosity. These

results indicate that for these values the assumption of cylindrical shape and statistical orientation for the pores as well as for the solid phase was not justified. Other shapes can be formed easily by powder metallurgical procedures like coextrusion or hot pressing for example. These techniques can also lead to oriented structures. Together, both the shape and the orientation factor can change in such a way that the right hand side of the curve in fig. 1 may be shifted to higher or lower values.

There are some new measurements given in the literature [29]) which are not included in fig. 1. The reason for this is the fact that the stereometric factors for the (U, Pu)O_2 material concerned are not given. On the other hand, the assumption of spherical or cylindrical pores would not be justified at all by the available information. In this context it is worth, mentioning that microcracks can be considered as oblate pores (lamellae), so that their influence on the conductivity can be calculated with the equations given above.

In fig. 2 the same comparison between a theoretical curve and experimental data is made for UN. The data are taken from the work of Kikuchi et al. [2]), who also determined by excellent measurements the portions of closed and open porosity in their specimens [2]). Therefore the ranges of porosity for which either eq. (6) ($P<10\%$) or eq. (7) had to be used

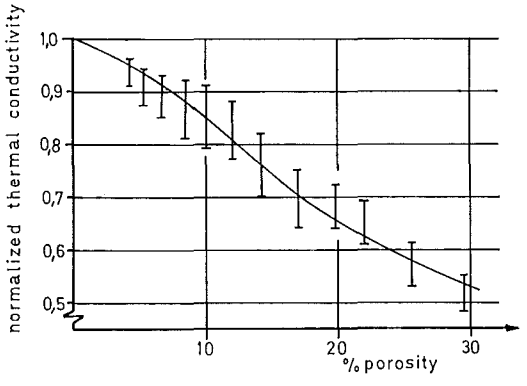


Fig. 2. The dependence of the normalized thermal conductivity of UN on porosity: $\mathbf{I}$: experimental values of Kikuchi et al., —: theoretical curve.

were fixed. In order to normalize the thermal conductivities at different amounts of porosity the values for dense UN were needed. They were gained by extrapolation of the curves of Kikuchi et al. showing the dependence of the thermal conductivity on porosity at different temperatures.

The extrapolated values agree closely with those measured for arc-melted UN [3]). Concerning the pore form and orientation the same factors were used as in the case of UO_2 (see fig. 1). As shown in fig. 2 the agreement between the experimental data and the theoretical curve is good.

3. Conclusion

The equations proposed in order to calculate the dependence of the thermal conductivity on porosity are useful to describe the slope of thermal conductivity curves for nuclear fuels containing nonconducting pores. There is a clear effect of the shape and the orientation of the pores on the thermal conductivity. This effect can be calculated for specific microstructures by using measured stereometric data from the planes of polish [12, 20, 21, 23]). The stereometric factors concerning shape and orientation of the pores in the proposed equations are independent of any parameters such as temperature, density etc. except those related to the geometry and geometrical arrangement of the porous material.

Considering the case of conducting pores, or more generally the case of two-phase materials, one has to return to the general equations of Niesel [16, 19, 20, 25]). One of them is valid for matrix-structured material corresponding to closed, isolated pores. The other one is valid for penetration type structured material corresponding to interconnected porosity. The equations considered here are valid either for nonconducting pores or two-phase material, in which a large difference exists between the thermal conductivities of the phases ($k_1/k_2 \to 0$). In the latter case a successful comparison between the experimental

and theoretical data has already been performed by using cermets as an example [25]).

In addition to the shape and orientation factors there exist three other stereometric factors: size, number and distribution of the phase constituents present in the material [24]). Size and number are included in the dependence of the thermal conductivity on concentration. The distribution, however, was taken to be statistical and constant in all cases considered above due to the fact that no useful quantitative criteria for the degree of distribution exists in theoretical equations up to now.

Acknowledgement

The authors greatly appreciate the helpful discussions with Prof. M. B. Waldron.

References

1) L. A. Goldsmith and J. A. M. Douglas, J. Nucl. Mater. 43 (1972) 225
2) T. Kikuchi, T. Takahashi and S. Nasu, J. Nucl. Mater. 45 (1972/1973) 284
3) Y. Takahashi, M. Murabayashi, Y. Akimoto and T. Mukaibo, J. Nucl. Mater. 38 (1971) 303
4) G. P. Marino, J. Nucl. Mater. 38 (1971) 178
5) R. L. Gibby, J. Nucl. Mater. 38 (1971) 163
6) J. C. van Craeynest and J. P. Stora, J. Nucl. Mater. 37 (1970) 153
7) J. C. Maxwell, Treatise on Electricity and Magnetism, Vol. 1 (Oxford University Press Oxford, 1873/1904)
8) E. E. Underwood, Quantitative Stereology (Addison-Wesley, New York 1970) p. 83
9) W. D. Kingery, J. Am. Ceram Soc. 42 (1959) 617
10) H. Kämpf and G. Karsten, Nucl. Appl. Techn. 9 (1970) 288
11) A. Eucken, VDI-Forschungsheft 353 (1932) 6
12) G. Ondracek and B. Schulz, Berichte DKG 48 (1971) 427
13) A. Biancheria, Trans. Am. Nucl. Soc. 9 (1966) 15
14) O. Wiener, Abh. der math.-phys. Klasse der königl.-sächsischen Ges. d. Wiss. Bd. 32 Nr.VI (1912) 509
15) H. Fricke, Phys. Rev. 24 (1924) 575
16) G. Ondracek and B. Schulz in Ber. des Kernforschungszentrums Karlsruhe, KFK 1272/3 (1972) 1126
17) D. A. G. Bruggeman, Ann. der Phys. 24 (1935) 636
18) D. A. G. Bruggeman, Ann. der Phys 25 (1936) 645
19) W. Niesel, Ann. der Phys. 6 (1952) 336
20) G. Ondracek and B. Schulz, Berichte DKG 48 (1971) 525
21) G. Ondracek and B. Schulz, Prakt. Metallographie 10 (1973) 16
22) S. Nazaré and G. Ondracek, The Microscope, 21 (1973) 49
23) G. Ondracek and B. Schulz, Prakt. Metallographie, Pt. 2 and 3 (1973) to be published
24) G. Ondracek, in: Science in Ceramics, Dt. Keram. Soc./Assoc. Europ. Ceram., in press
25) S. Nazaré, G. Ondracek and F. Thümmler, in: H. H. Hausner, Modern Developments in Powder Metallurgy, vol. 5 (Plenum Press New York, 1971) p. 171
26) E. M. Müller, Atomwirtschaft, September/Oktober (1970) p. 434
27) A. E. Powers, KAPL-2145/TUD (1970) 16th ed.
28) G. Ondracek, Berichte DKG, to be published (1973)
29) R. L. Gibby, HEDL-TME-72-88 (1972)
30) B. Schulz, Diss. Univ. Karlruhe, in preparation (1973)