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ON THE TEMPERATURE DEPENDENCE OF THE COEFFICIENT OF THERMAL CONDUCTIVITY OF POLYCRYSTALLINE $ZnCr_2O_4$ AND $MgCr_2O_4$

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Abstract: *The coefficient of thermal conductivity of polycrystalline zinc and magnesium chromite samples was measured from room temperature to 300° C by the comparative method and was found to be of the order of 10^{-3} cal/sec—deg—cm, varying very slowly with temterature in this range.*

INTRODUCTION

The coefficient of thermal conductivity k of a material is defined by the equation

$$\frac{\dot{Q}}{A} = -k\vec{\nabla}T,$$

where $\dot{Q}$ is the rate of heat flow perpendicularly through the surface A, and $\vec{\nabla}T$ is the temperature gradient. For a certain material k depends on its chemical composition, its physical properties and on temperature.

The determination of k of an industrial material is important for two reasons. First, from a theoretical point of view, it contributes to the better understanding of the structure of the material and second, from a practical point of view, a rough knowledge of its value is necessary for the design of instruments and experimental setups which make nse of the material.

Experimentally, k can be determined by static and dynamic methods in which the temperature distribution is, respectively, constant or

changing with time. In addition, absolute or comparative methods can be used.

Accurate measurements of k are difficult, given the small difference in its value in the best thermal insulator and the best thermal conductor. It is evident that it is much more difficult to isolate a sample thermally than electrically.

The materials studied in this paper are two chromite spinels, $ZnCr_2O_4$ and $MgCr_2O_4$. They are hoth refractory materials and they can be found in chrome ores. The relative ease with which they form solid solutions with other spinels makes them useful in the preparation and study of ferrites. Also, mixed with magnetite, they can be used for the manufacturing of materials of controlled electrical conductivity[13].

$ZnCr_2O_4$ ($\alpha = 8.3275$ Å, M. W. $= 233.40$ gm, d $= 5.366$ gm/cm^3) has a stable normal structure at room temperature due to the strong octahedral site preference of Cr^{+3} and the strong tetrahedral site preference of Zn^{+2}[12]. Reported values in the literature of its Debye temperature are 670° K[5] from infrared data and 550° K[1] from neutron diffraction data. Zinc chromite is paramagnetic at room temperature with $T_{Neel} = 16°$ K[1] and asymptotic Curie temperature equal to —350° K[9]. The d.c. conductivity is of the order of 10^{-10} Ohm^{-1}·cm^{-1}[13].

The properties of $MgCr_2O_4$ ($\alpha = 8.333$ Å, M.W. $= 192.34$ gm, d $=$ 4.414 gm/cm^3) are similar to those of $ZnCr_2O_4$. It also has a stable normal structure[12]. The reported values of its Debye temperature from infrared data is 687° K and about 340° K from the Debye - Waller factor[5]. The Néel temperature is 15° K[2] and the asymptotic Curie temperature is —370° K[9]. The d.c. electrical conductivity is of the order of 10^{-12} Ohm^{-1}· cm^{-1}[13].

PREPARATION OF SAMPLES

Chromites are described by the general formula $MeCr_2O_4$. The samples which were used for our measurements were prepared by the mixed oxide method which consists of mixing molar quantities of the oxides MeO ($Me^{+2} = Zn^{+2}$, Mg^{-2}) and Cr_2O_3 in a ball mill, pressing and heating to a high temperature for extended periods of time.

Two samples of $ZnCr_2O_4$ and one sample of $MgCr_2O_4$ were prepared. Zinc chromite Sample No 1 was pressed under 4200 psi at 85° C and heated at 1110° C. Zinc Chromite Sample No 2 was pressed under 9450 psi at 85° C and heated at 1200° C. The magnesium chromite sample was

pressed under 9450 psi at room temperature and heated at 1250° C. Zinc chromite samples 1 and 2 had a porosity of 8.3% and 8.7%, respectively whereas the magnesium chromite sample had a porosity of 23.2%. The structure of the materials was checked by X-ray diffraction giving a lattice constant of 8.35 Å and 8.33 Å for the zinc and magnesium chromites respectively.

All the samples were light green in colour, cylindrical in shape, with a diameter of one inch, and a height of half an inch. Results of measurements of their d.c. electrical conductivity as a function of temperature were comparable to those quoted by earlier investigators[13].

EXPERIMENTAL PROCEDURE

In order to measure the coefficient of thermal conductivity of a given sample it is necessary to know the heat current flowing through the sample and the temperature on the sample along the path of the current.

At high temperatures, the heat losses being considerable, apart from being radiated from the lateral surface of the sample, a large part of the heat produced by the heaters is lost before it enters the sample, thus causing an inaccurate determination of $\dot{Q}$. This can be avoided by the use of the comparative method in which only the temperature at certain points along the unknown and a reference sample need be measured.

In our measurements we used the comparative method, with fused quartz as the reference material. The quartz sample was obtained from Thermal Syndicate Ltd. and the values of its thermal conductivity as a function of temperature were taken from Devyamkova et al.[3].

In a system of two samples, one on top of the other, ignoring lateral heat losses and assuming the isothermal surfaces to be perpendicular to the heat flow, one can write $\dot{Q}_{unknown} = \dot{Q}_{reference}$. Therefore, for small temperature gradients,

$$k_{unknown} = k_{reference} \frac{\left(\frac{\Delta T}{\Delta y}\right)_{reference}}{\left(\frac{\Delta T}{\Delta y}\right)_{unknown}}$$

As a result of the assumptions made in the derivation of the above relationship, in practice one must watch against thermal contact re-

sistance and lateral heat losses. For this purpose, the following precautions were taken:

i) a smaller than unity sample height to sample diameter ratio was chosen to reduce heat losses from the lateral surface,

ii) the measurements were conducted in vacuum and the lateral surface of the samples was blackened to reduce heat radiation losses,

iii) a guard heater was used in order to match the temperature distribution of the environment to that of the samples, and

iv) thin copper plates were placed on the sample surfaces and the whole system, consisting of heaters, copper plates, and samples, was pressed together for better thermal contact and for keeping the heat flow homogeneous.

The experimental setup is shown in figure 1. Three copper - constantan thermocouples were used for the measurement of temperature on the sample surfaces. These were placed in slots on the copper plates with their tips coinciding with the axis of the cylindrical samples. A running water cooling system was used as a heat sink. Two kanthal heaters acted one as the main heater, producing the heat current, and the other as an auxilliary heater, keeping the temperature gradient small while the temperature level was raised.

The guard heater consisted of a quartz tube surrounding the samples and in contact with both heaters, being heated at top and bottom by a turn of kanthal wire each in series with the respective heater.

The temperature of the environment of the samples was measured by an additional copper-constantan thermocouple and was controlled by a furnace which, in turn, was surrounded by a metallic cover. The whole system was placed in a glass bell and connected to a mechanical vacuum pump.

The measurements, taken during consecutive heating and cooling of the samples, consisted of taking the temperature of the sample surface and of the environment, after temperature equilibrium had been obtained. Each result given in the tables is the average of eight to ten measurements.

RESULTS

The results which were obtained for two zinc chromite samples and one magnesium chromite sample are shown in the following tables and figures. In zinc chromite Sample No 1 (Fig. 2) a peak was observed in k

near 150° C during the first heating, but disappeared during subsequent heating and cooling (Fig. 3). This was probably due to ordering of cations in samples which had not been cooled slowly enough when they were prepared.

As L. A. Reznitskii[10] observed, zinc chromite has a partly inverted structure at high temperatures which is retained if the sample is quenched or cooled quickly. Due to the great affinity of Cr^{+3} for the octahedral sites, an ordering takes place between 147° C and 397° C during subsequent slow heating of the sample and the material reverts to the perfectly normal structure. The presence of thermal hysteresis (Fig. 3) indicates the presence of microcracks in the sample.

Zinc chromite Sample No 2 (Fig. 4) had been heated slowly before being subjected to measurements and only a small rise in k was observed near 150° C.

With respect to the magnesium chromite sample a similar peak in k was observed at the first heating near 100° C (Fig. 5), after which the results were repeatable (Fig. 6).

In both materials the variation of k with temperature was very small.

DISCUSSION

The finite value of the coefficient of thermal conductivity of ceramic dielectric materials is the result of the inelastic scattering of phonons with other phonons (umklapp scattering), with sample and grain boundaries, and with impurities, and depends on the phonon contribution to the specific heat per unit volume and on the phonon velocity and mean free path. The total thermal conductivity can be written as

$$\frac{1}{k} = \sum_i \frac{1}{k_i},$$

where the subscript i represents the different scattering processes.

Of the scattering processes mentioned above the ones effective at intermediate ($\Theta_D/3<T<\Theta_D$) and high ($T>\Theta_D$) temperatures are umklapp and impurity scattering. At high temperatures umklapp scattering causes an $1/T$ variation of k, while the effect of impurity scattering is independent of temperature, there being no such simple temperature dependence of scattering processes in the intermediate temperature region.

In the case of ceramic materials the study of thermal conductivity is further complicated by the presence of other materials in solid solution and by the presence of other phases, one of which can be porosity[4,7,8].

The presence of impurity atoms in solid solution causes a reduction in the value of thermal conductivity which depends on the mass, size and binding energy difference of the impurity. The effectiveness of a second phase in affecting the thermal conductivity of a ceramic material depends on the relative conductivity and on the distribution of the second phase. Since porosity can be considered as an individual phase it must be taken into account. It has been found that if porosity is randomly dispersed in a continuous solid phase, for temperatures lower than 500° C, the thermal conductivity of a material can be described by the relationship $k = k_m/1-P$ where P is the pore fraction and k_m is the measured value of k.

The thermal conductivity of the materials examined in this paper is expected to be low considering their complex structure and polycrystalline form. They are also expected to contain impurities which were introduced either by the starting materials (purity 99%) or in some preparation stage i.e. milling. In addition to porosity other phases can be expected to be present from the incomplete reaction of the oxides.

Since the reported values of the Debye temperature of these chromites place the temperature region in which measurements were conducted in the intermediate region ($T \lesssim \Theta_D$), no theoretical prediction of k can be made. The thermal conductivity of these materials has not been measured before, except for measurements conducted on the coefficient of thermal conductivity of chromite bricks[11] and of mixed chromite spinels[14] which have results of the same order of magnitude as those obtained by our measurements on zinc and magnesium chromite.

The values, corrected to zero porosity, obtained at 200° C for k of $ZnCr_2O_4$ are $3{,}74 \times 10^{-3}$ cal/cm·sec·deg and $3{,}92 \times 10^{-3}$ cal/cm·sec·deg respectively, the value of k of $MgCr_2O_4$ being higher than that of $ZnCr_2O_4$, as expected due to the magnesium ion being lighter than the zinc ion. Also, as expected, the values of k of $ZnCr_2O_4$ and of $MgCr_2O_4$ are lower than the respective values of ZnO and MgO[6] because of their more complex structure. Unfortunately, there seems to be no comparable data available in the literature, concerning Cr_2O_3.

Disregarding the problem arising from the difficulty in predict-

ing the thermal conductivity of a material near and below the Debye temperature, and from the difficulty in isolating a sample thermally, k can be measured with greater accuracy only if samples of great purity and homogeneity are prepared. Without samples of controllable physical characteristics, at least for ceramic materials, only a rough knowledge of the thermal conductivity can be achieved.

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TABLE I

The coefficient of thermal conductivity of $ZnCr_2O_4$.

Sample No. 1 (First heating)		Sample No. 1 (Upper curve)		Sample No. 1 (Lower curve)		Sample No. 2	
T(°C)	k(cal/cm·sec·deg)	T(°C)	k(cal/cm·sec·deg)	T(°C)	k(cal/cm·sec·deg)	T(°C)	k(cal/cm·sec·deg)
33	3.37	113	3.95	40	3.85	82	3.25
39	3.35	120	3.94	46	3.81	105	3.24
47	3.32	124	3.94	57	3.88	127	3.35
58	3.31	136	3.87	66	3.91	150	3.48
68	3.27	147	3.82	70	3.80	160	3.35
79	3.28	150	3.83	85	3.67	170	3.31
92	3.28	162	3.83	93	3.62	185	3.40
101	3.28	170	3.82	99	3.61	205	3.34
110	3.30	177	3.71	104	3.60	226	3.25
121	3.34	197	3.66	125	3.66	245	3.16
132	3.39	213	3.59	184	3.54	265	3.04
140	3.47	227	3.41	197	3.52	289	3.03
145	3.51	245	3.26	252	3.23		
154	3.88	255	3.26	286	3.08		
185	3.81	267	3.17				
204	3.73	278	3.16				
215	3.69	290	3.09				
219	3.68	307	3.10				
230	3.61	319	3.05				
245	3.60						

TABLE II

The coefficient of thermal conductivity of $MgCr_2O_4$.

First heating		Curve No. 1		Curve No. 2		Curve No. 3		Curve No. 4	
T(°C)	k $\frac{cal}{cm \cdot sec \cdot deg}$	T(°C)	k $\frac{cal}{cm \cdot sec \cdot deg}$	T(°C)	k $\frac{cal}{cm \cdot sec \cdot deg}$	T(°C)	k $\frac{cal}{cm \cdot sec \cdot deg}$	T(°C)	k $\frac{cal}{cm \cdot sec \cdot deg}$
37	3.30	57	2.65	37	2.63	58	2.81	47	2.79
46	3.37	67	2.66	45	2.65	69	2.89	59	2.81
59	3.47	85	2.75	58	2.69	89	2.93	71	2.84
67	3.55	108	2.83	67	2.74	110	2.96	89	2.89
83	3.58	132	2.80	82	2.78	136	2.96	112	2.92
107	3.63	148	2.90	107	2.86	151	2.99	139	2.94
131	3.15	218	2.85	137	2.88	192	2.87	157	2.98
153	3.05	267	2.77	157	2.92				
192	3.00			194	2.85				
218	2.99			225	2.80				
247	2.93								
273	2.85								
307	2.80								

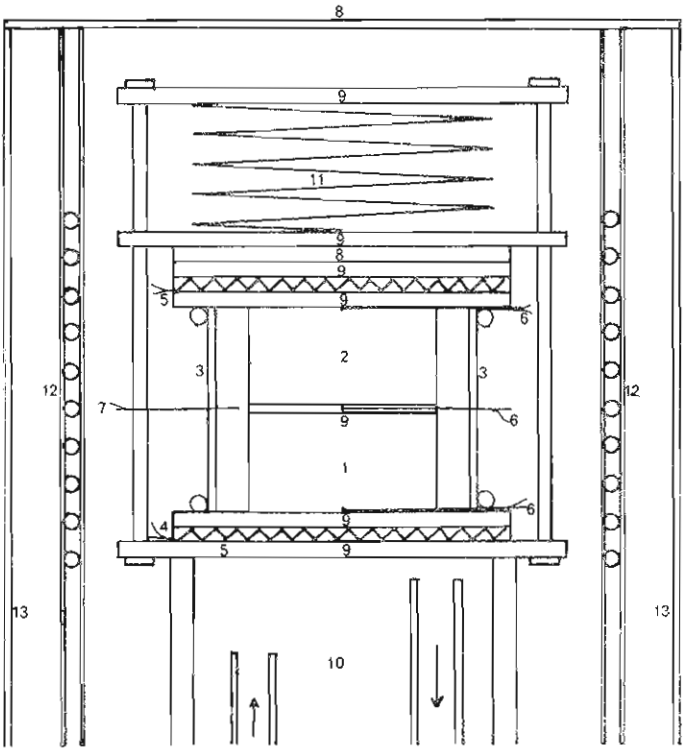

Fig. 1: Apparatus for measuring the coefficient of thermal conductivity of zinc and magnesium chromites.

1. Chromite sample, 2. Fused quartz sample, 3. Guard heater quartz tube, 4. Auxiliary kanthal heater, in series with one turn of kanthal wire at the bottom of the guard heater tube, 5. Main kanthal heater, in series with one turn of kanthal wire at the top of the guard heater tube, 6. Copper-constantan thermocouples inside radial slots in copper plates, 7. Copper-constantan thermocouple measuring the temperature of the environment near the interface of the two samples, 8. Asbestos foil, 9. Copper plates, 10. Water cooling system, 11. Spring, 12. Furnace, 13. Aluminium shield.

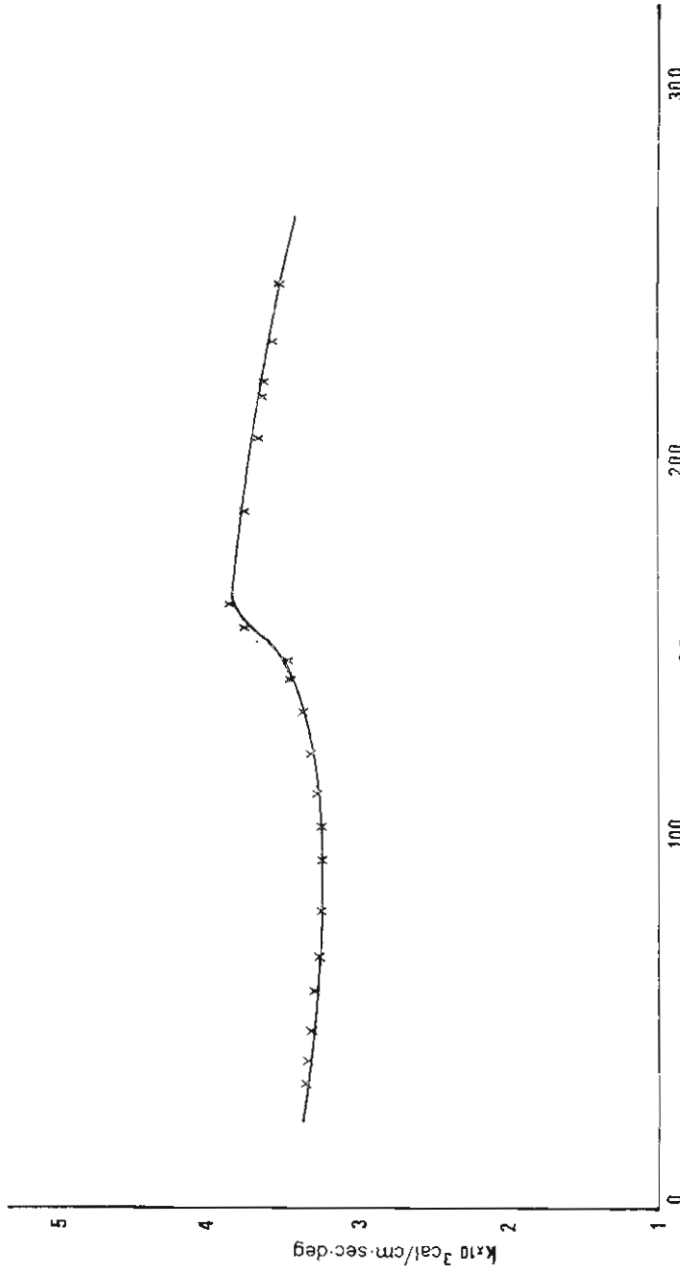

Fig. 2: Temperature dependence of the coefficient of thermal conductivity of $ZnCr_2O_4$. (Sample No. 1, First heating).

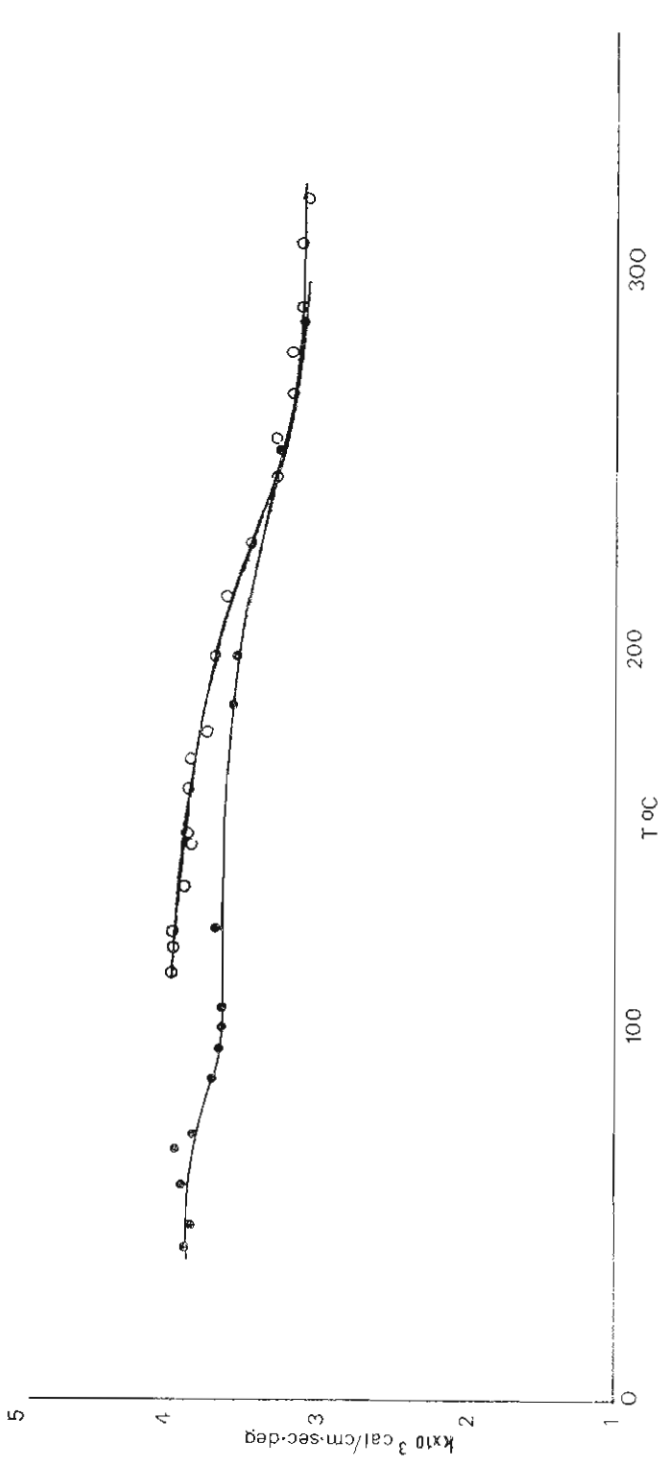

Fig 3: Temperature dependence of the coefficient of thermal conductivity of $ZnCr_2O_4$. *(Sample No. 1).*

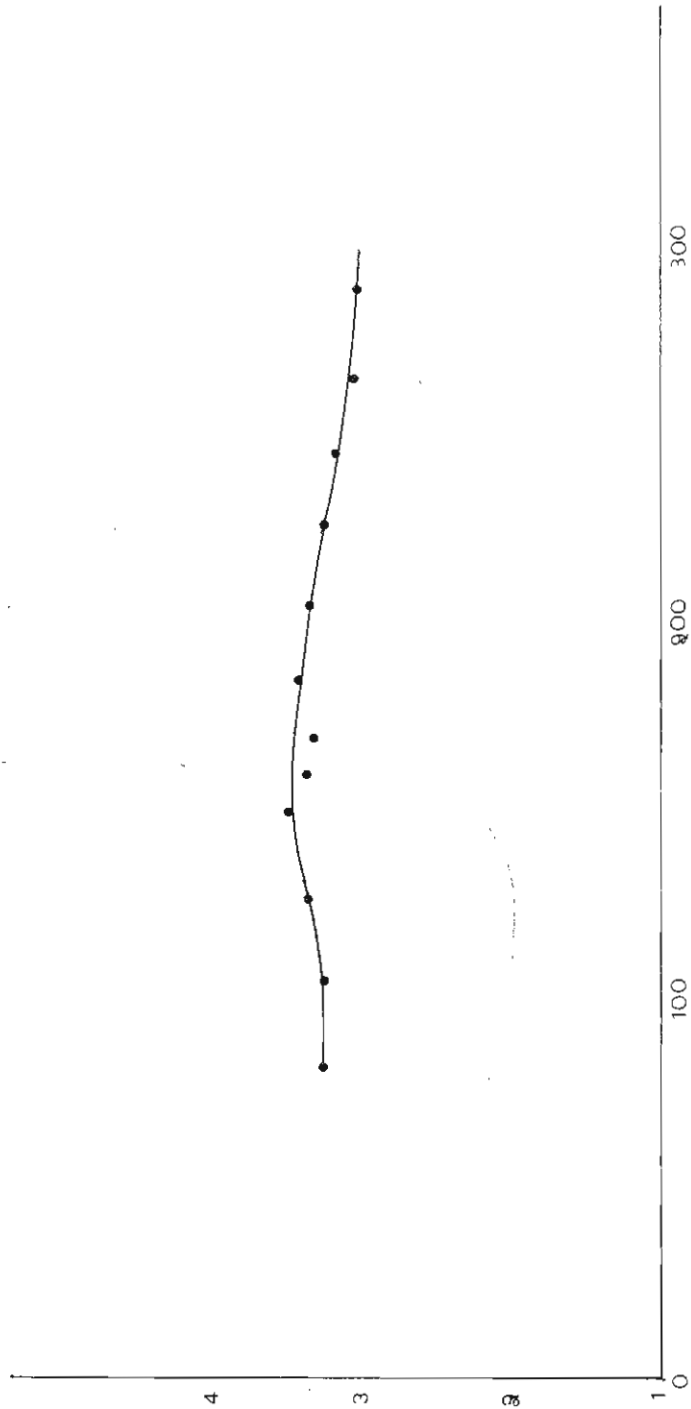

Fig 4: Temperature dependence of the coefficient of thermal conductivity of $ZnCr_2O_4$. (Sample No. 2).

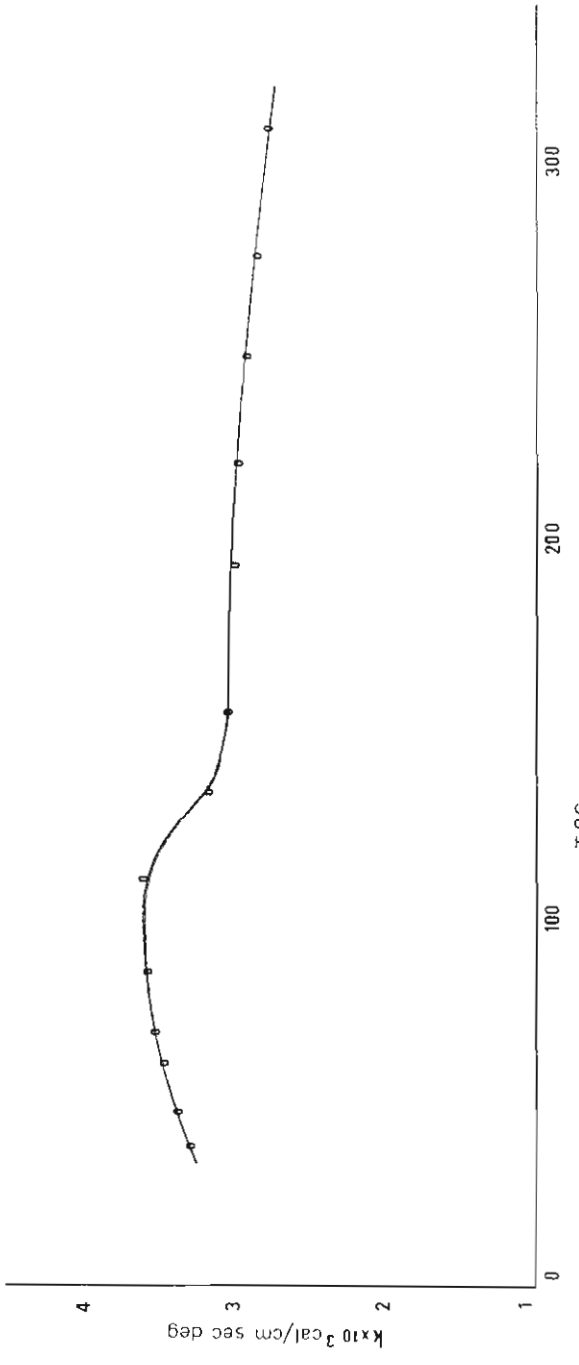

Fig. 5: Temperature dependence of the coefficient of thermal conductivity of $MgCr_2O_4$. (First heating).

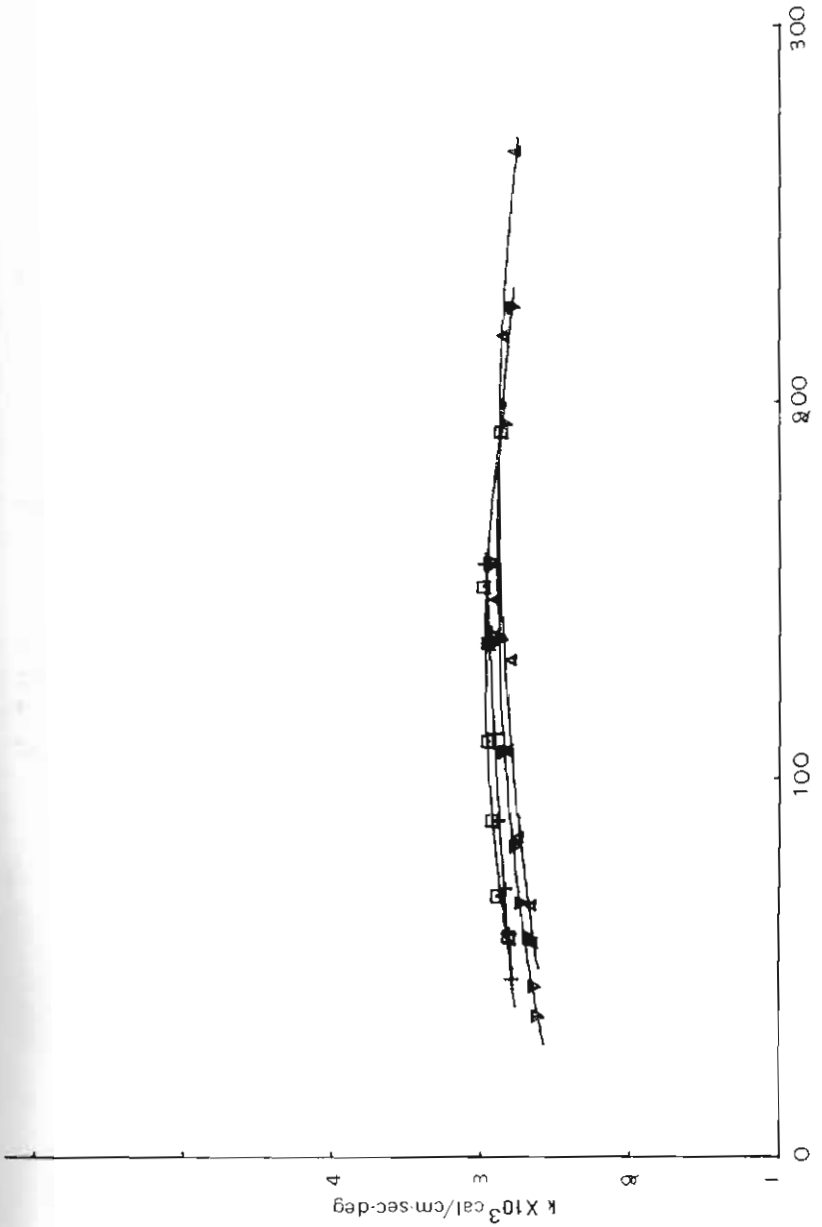

Fig. 6: Temperature dependence of the coefficient of thermal conductivity of $MgCr_2O_4$.

ΠΕΡΙΛΗΨΗ

Ο ΣΥΝΤΕΛΕΣΤΗΣ ΘΕΡΜΙΚΗΣ ΑΓΩΓΙΜΟΤΗΤΟΣ ΣΥΝΑΡΤΗΣΕΙ ΤΗΣ ΘΕΡΜΟΚΡΑΣΙΑΣ, ΣΕ ΠΟΛΥΚΡΥΣΤΑΛΛΙΚΑ ΔΕΙΓΜΑΤΑ $ZnCr_2O_4$ ΚΑΙ $MgCr_2O_4$

Ὑπὸ

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Ἔγιναν μετρήσεις τοῦ συντελεστοῦ θερμικῆς ἀγωγιμότητος σὲ πολυκρυσταλλικὰ δείγματα χρωμιτῶν ψευδαργύρου καὶ μαγνησίου, ἀπὸ τὴν θερμοκρασία δωματίου μέχρι 300° C. Χρησιμοποιήθηκε ἡ συγκριτικὴ μέθοδος καὶ ὁ συντελεστὴς θερμικῆς ἀγωγιμότητος βρέθηκε νὰ εἶναι τῆς τάξεως 10^{-3} cal/cm·sec·deg, μεταβαλλόμενος ἐλάχιστα συναρτήσει τῆς θερμοκρασίας σ' αὐτὴ τὴν περιοχὴ θερμοκρασιῶν.