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16.Summary/Notes

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ON THE USE OF THE PHOTOACOUSTIC EFFECT FOR INVESTIGATING PHASE-TRANSITIONS IN SOLIDS

by

* M.A.A. Siqueira, C.C. Ghizoni

** J.I. Vargas

*** E.A. Menezes, H. Vargas and L.C.M. Miranda

ABSTRACT

By exploring the dependence of the photoacoustic signal on the thermal properties of the sample, we demonstrate experimentally the usefulness of the photoacoustic effect for investigating phase-transitions in solids. Special application is made for the case of Al-doped VO_2. We also describe the photoacoustic cell utilized and the complete characterization of the cell is done by using a piece of Germanium in single crystal form which has well known thermal properties.

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* Conselho Nacional de Desenvolvimento Científico e Tecnológico - Instituto de Pesquisas Espaciais, São José dos Campos, SP, Brazil.

** Universidade Federal de Minas Gerais - Departamento de Química - Belo Horizonte, MG, Brazil.

*** Universidade Estadual de Campinas - Instituto de Física - Campinas, SP, Brazil.

The basic principles of the photoacoustic (PA) effect in solid samples are by now well established[1-3]. The primary source of the acoustic signal is the periodic heat flow from the sample to the surrounding gas, as the solid is cyclically heated by the absorption of chopped light. The periodic flow of this heat into the gas cell produces pressure fluctuations which are detected as an acoustic signal. In this energy-conversion process (light into sound), the thermal properties of the sample play an important role. This suggests the possibility of using the photoacoustic effect for the study of the thermal properties of solids[4], such as the thermal conductivity and the specific heat.

In this paper we report the use of the photoacoustic effect for investigating phase-transitions in solid samples. To see how this can be accomplished, let us go back to Rosencwaig and Gersho's (RG) theory[5] and consider, for sake of argument, the simple case of an optically opaque and thermally thick sample. Under these circunstances, the PA signal Q independs of the optical absorption coefficient β and can be written as[5].

$$Q = Af(T)/\left[C_s(T)\, K_s(T) \right]^{1/2} \qquad (1)$$

where A is a conversion coefficient, reflecting all the factors, independent of the temperature T in the generation of the PA signal. The function f(T) accounts for all the thermal properties of the cell and internal gas, and $C_s(T)$ and $K_s(T)$ are the specific heat at constant pressure and the thermal conductivity of the sample, respectively. It follows from Eq. (1) that, by varying the temperature, the PA signal should exhibit a sudden decrease as the specific heat jumps at the transition temperature.

In the following, we demonstrate this effect by studying the temperature dependence of the PA signal of policrystalline

0.8 at % Al-doped VO_2 sample. The choice of this material, as the working sample, was dictated by the condition of having an optically opaque and thermally thick sample using visible radiation modulated at a frequency of 200 Hz. It should, however, be emphasized here that this is not a restriction of the method itself, but rather a simplifying condition for quantitative analysis. In Fig. 1 we present the PA signal dependence on the temperature of the Al-doped VO_2 sample. This curve already suggests the existence of a second order phase transition with a transition temperature (T_n) around 47°C.

The experimental set-up is displayed in Fig. 2. The light source is a tungsten lamp with a filter to cut the contribution from wavelenghts greater than 1 μm, chopped at 200 Hz. Since the energy gap of this sample[6], at room temperature, is at about 2 μm, the absorption of light by the sample can be assumed to be saturated (ie, β is constant) for the visible light. Even if the absorption coefficient is not saturated and is varying with the temperature, it would have no effect on the PA signal due to its large value relative to the thermal diffusion coefficient (a_s) of the sample. This is essentially the condition of an optically opaque and thermally thick sample according to RG theory[5]. To make sure that this was actually the case, we have measured the PA signal at fixed temperature, as a function of the chopping frequency. This result is shown in Fig. 3. The PA signal so obtained depends linearly on the inverse of the chopper frequency which indicates that the absorption coefficient is larger than the thermal diffusion coefficient according to RG theory (see Eq(27) of Ref. 5). Finally, a few words about the sample heating is in order. The specially designed cell shown in Fig. 4 has two heater windings to allow an uniform temperature distribution in the sample. The temperature of the sample was measured with a thermocouple and was plotted on the X-axis of X-Y recorder. This thermocouple was placed in close contact with the sample compartment trough a small hole in the cell body. The microphone, used as a tranducer, was placed in a separate chamber, refrigerated with flowing water in order

to prevent damaging. It is important to notice here that the heating of the sample has to be done adiabatically, otherwise convective heat flow will be established in the cell modifying considerably the PA signal.

To establish the existence of a phase-transition in the PA signal of Fig. 1 one should now calculate the quantity $C_s(T) \times K_s(T)$. Now, according to Eq. (1), we need to know first how the function f(T), a characteristic of the cell only, varies with the temperature. This was done by choosing Ge as our standard since its thermal properties are well known[7,8]. A piece of Ge single crystal was placed inside the cell and illuminated with white light. Care has been taken to make sure that its energy gap dependence on the temperature did not influence the PA signal. We used a yellow filter so that the red and near infrared portions of the spectrum were cut out. In Fig. 5, the results for the Ge crystal are presented in curve (a). The normalized value for f(T) was then calculated from the relation.

$$\bar{f}(T) = \frac{f(T)}{f(293)} = \left[\frac{C_s(T)\ K_s(T)}{C_s(293)\ K_s(293)} \right]^{1/2} \cdot \frac{Q(T)}{Q(293)} \qquad (2)$$

using the values of $C_s(T)$ and $K_s(T)$ for Germanium, taken from References 3 and 4. The resulting function $\bar{f}(T)$ is shown in curve (b) of Fig. 5.

As we have mentioned, the normalized function, $\bar{f}(T)$, completely characterizes the cell, so that thermal properties of different samples can be studied. Putting all these results together we can finally, calculate the curve $C_s(T)\ K_s(T)$ as a function of T for our Al-doped VO_2 sample from

$$\frac{C_s(T)\ K_s(T)}{C_s(293)\ K_s(293)} = \left[\frac{Q(293)}{Q(T)} \cdot \bar{f}(T)\right]^2 \qquad (3)$$

The results are shown in Fig. 6. Since the thermal conductivity $K_s(T)$ in Eq. (3) can be assumed to be a smooth function of the temperature, the jump, in Fig. 6, between 308° and 338°K is then attributed to the jump of the specific heat, defining therefore, a phase-transition at $T_n = 47 + 273 = 320^{\circ}K$. This value of T_n agrees very well with the NMR result[9] and corresponds to the transition from the (M_1) phase to the mixed ($M_1 + M_2$) phase of 0.8 at % Al-doped VO_2[9,10]. Furthermore, by looking more carefully at the structure of the plot in Fig. 6, between 343°K and 373°K, one is tempted to assign two other phase transitions: one between 343°K and 363°K, probably due to the transformation from the ($M_1 + M_2$) to the (M_2) phase, and the other one, between 363°K and 373°K, due to the transformation from (M_2) phase to the metallic (R) phase. However, in order to make this statement more definite, one needs to know the temperature dependence of the thermal conductivity of Al-doped VO_2, which, to our knowledge, is not available at the moment.

In conclusion, we have shown, in this paper, the usefulness of the photoacoustic effect for studying phase-transitions in solids[11], considering, as an example, the case of Al-doped VO_2. We believe this clearly demonstrate the great versatility of this simple technique. The reason for such usefulness of the photoacoustic effect is, in our opinion, the richness of information contained in the acoustic signal. The photoacoustic signal depends both on the optical and the thermal properties of the sample, as well as on its geometry. By this geometric effect (for powdered samples) we mean, for instance, the dependence of the PA signal on the shape of the sample. Both the sample-gas heat exchange efficiency[12] and the scattering of light[13] are changed by changing the sample size and shape, making therefore the PA signal size and shape dependent. Furthermore, this simple

principle of periodic heat flow from the sample to gas can also be explored, to investigate such diverse phenomena as the propagation and instability of sound in semiconductors[14].

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FIGURE CAPTIONS

Fig. 1 - Photoacoustic signal (Q) of 0.8 at % Al-doped VO_2 as a function of temperature (T) for white light illumination and chopping frequency of 200 Hz.

Fig. 2 - Block diagram of the experimental set-up for measuring the temperature dependence of the PA signal.

Fig. 3 - Photoacoustic signal (Q) of 0.8 at % Al-doped VO_2 as a function of the chopper period (τ) for white light illumination.

Fig. 4 - The PA cell for thermal studies:

1. Window assembly
2. Sample compartment
3. Cell body (anodized aluminium)
4. Thermocouple
5. External heater winding
6. Internal heater winding
7. Cooling assembly
8. Microphone and pre-amplifier compartment
9. Water inlet
10. Water outlet
11. Electrical connections

Fig. 5 - (a) Photoacoustic signal of Ge - single crystal as a function of the temperature (T) for white light illumination and chopping frequency of 200 Hz;

(b) Resulting normalized $\bar{f}(T)$ calculated according to Eq. (2) of the text.

Fig. 6 - Temperature variation of $C_s(T)\ K_s(T)$ of Al-doped VO_2, normalized to its value of 293^oK, calculated according to EQ. (3) of the text.

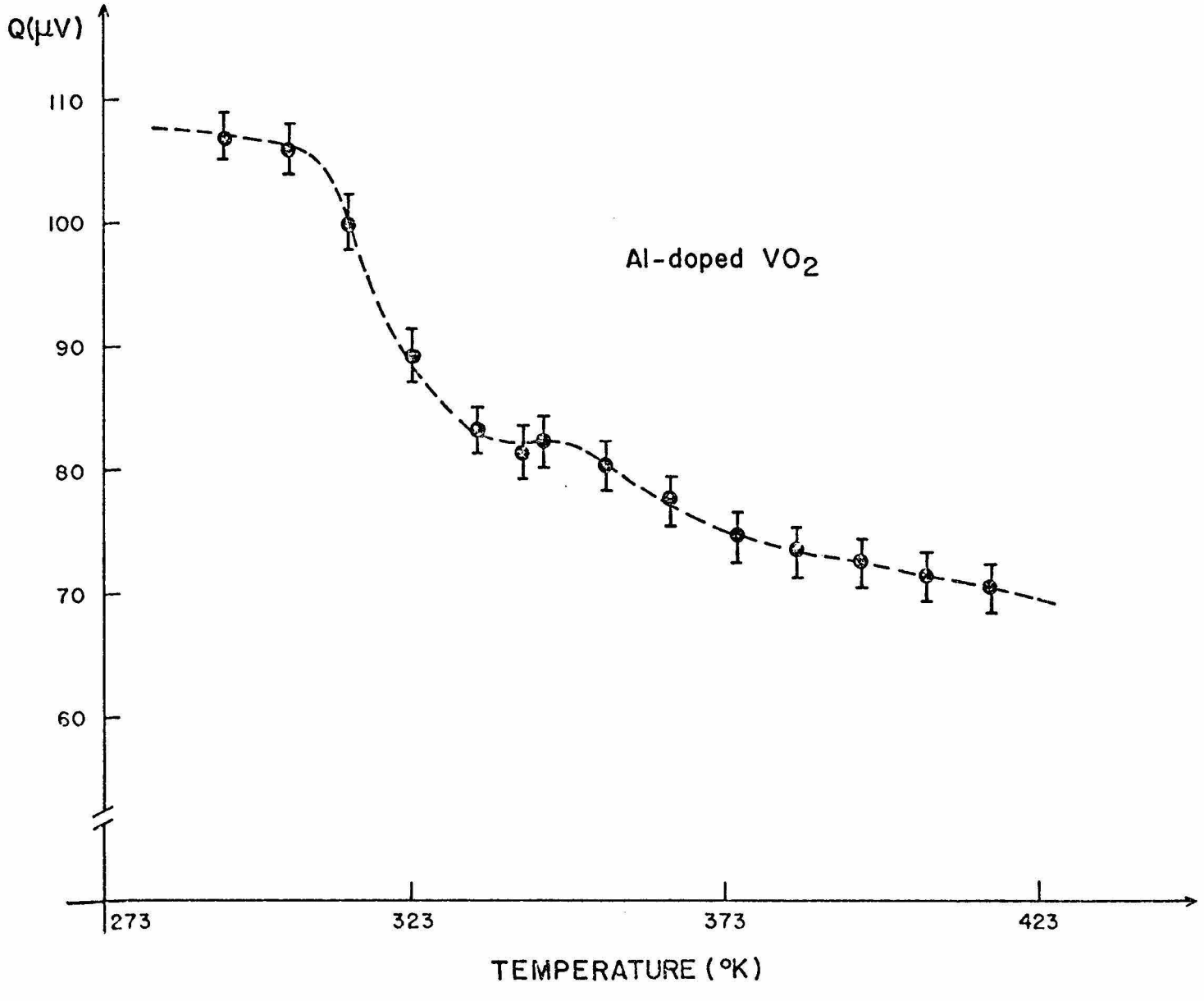
Q(μV)
110
100
90
80
70
60
Al-doped VO_2
273
323
373
423
TEMPERATURE (°K)

Fig. 1

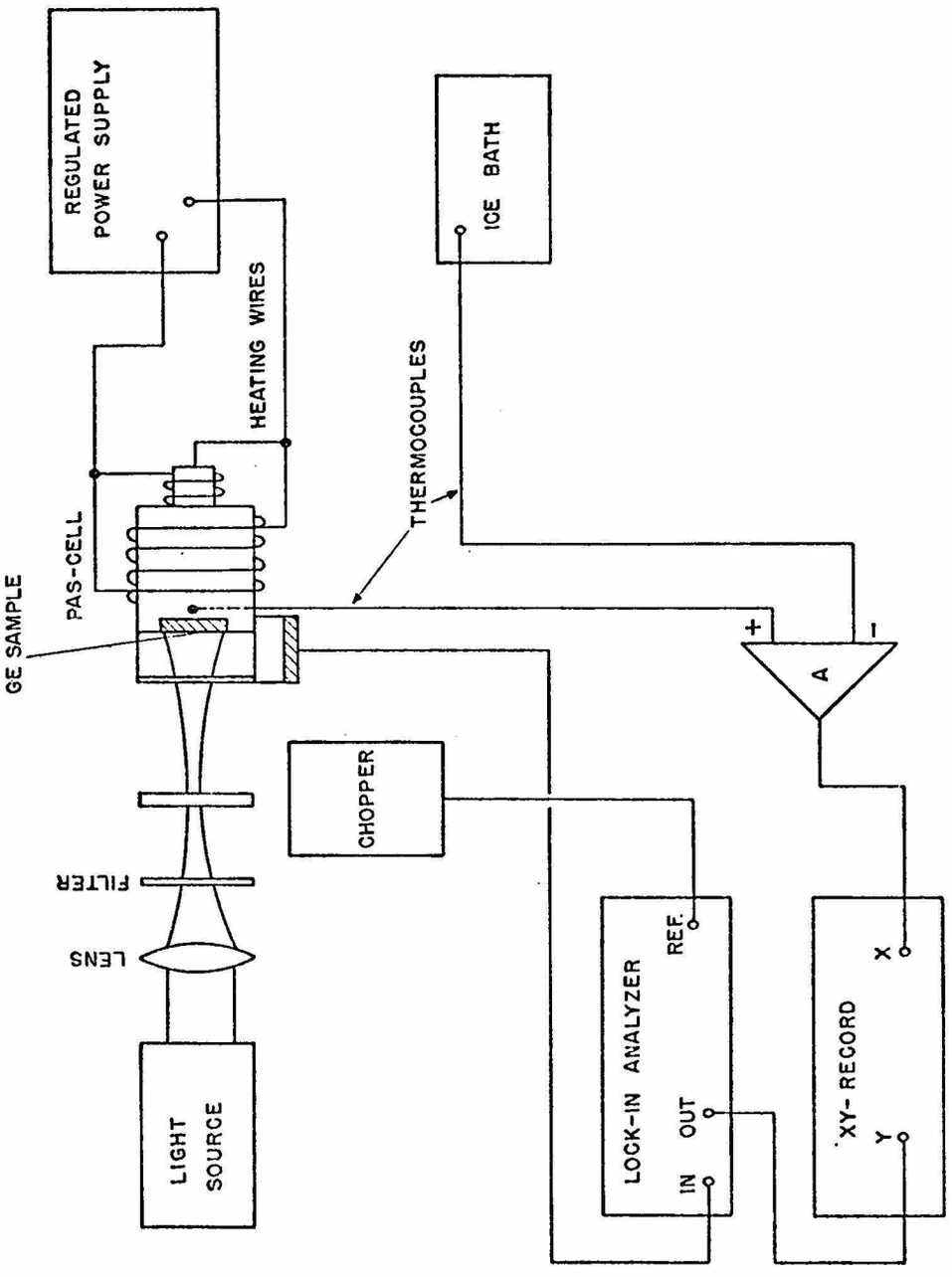
REGULATED POWER SUPPLY
ICE BATH
HEATING WIRES
THERMOCOUPLES
PAS-CELL
GE SAMPLE
+
-
A
CHOPPER
FILTER
LENS
LIGHT SOURCE
LOCK-IN ANALYZER
REF.
IN
OUT
XY- RECORD
X
Y

Fig. 2

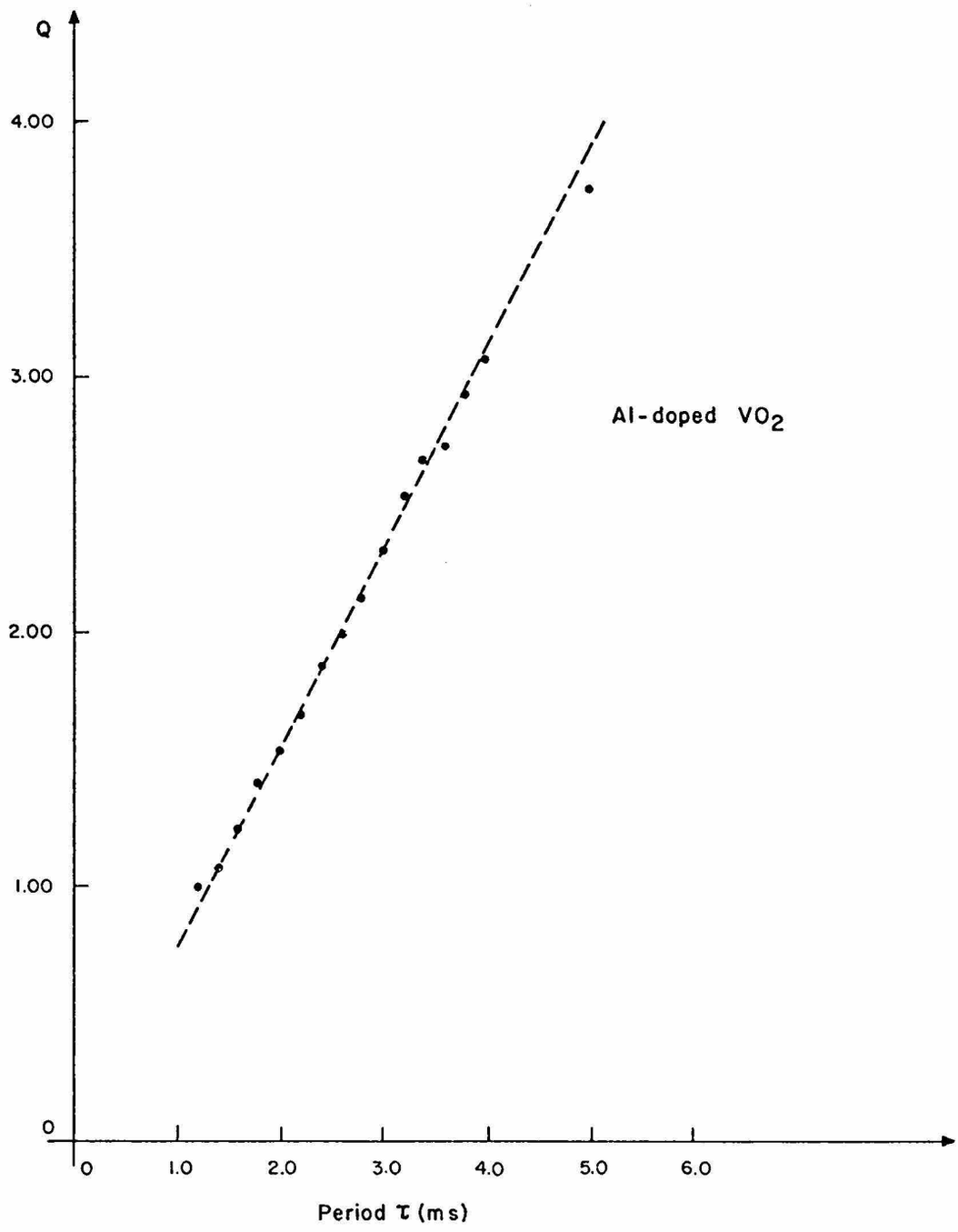

Fig. 3

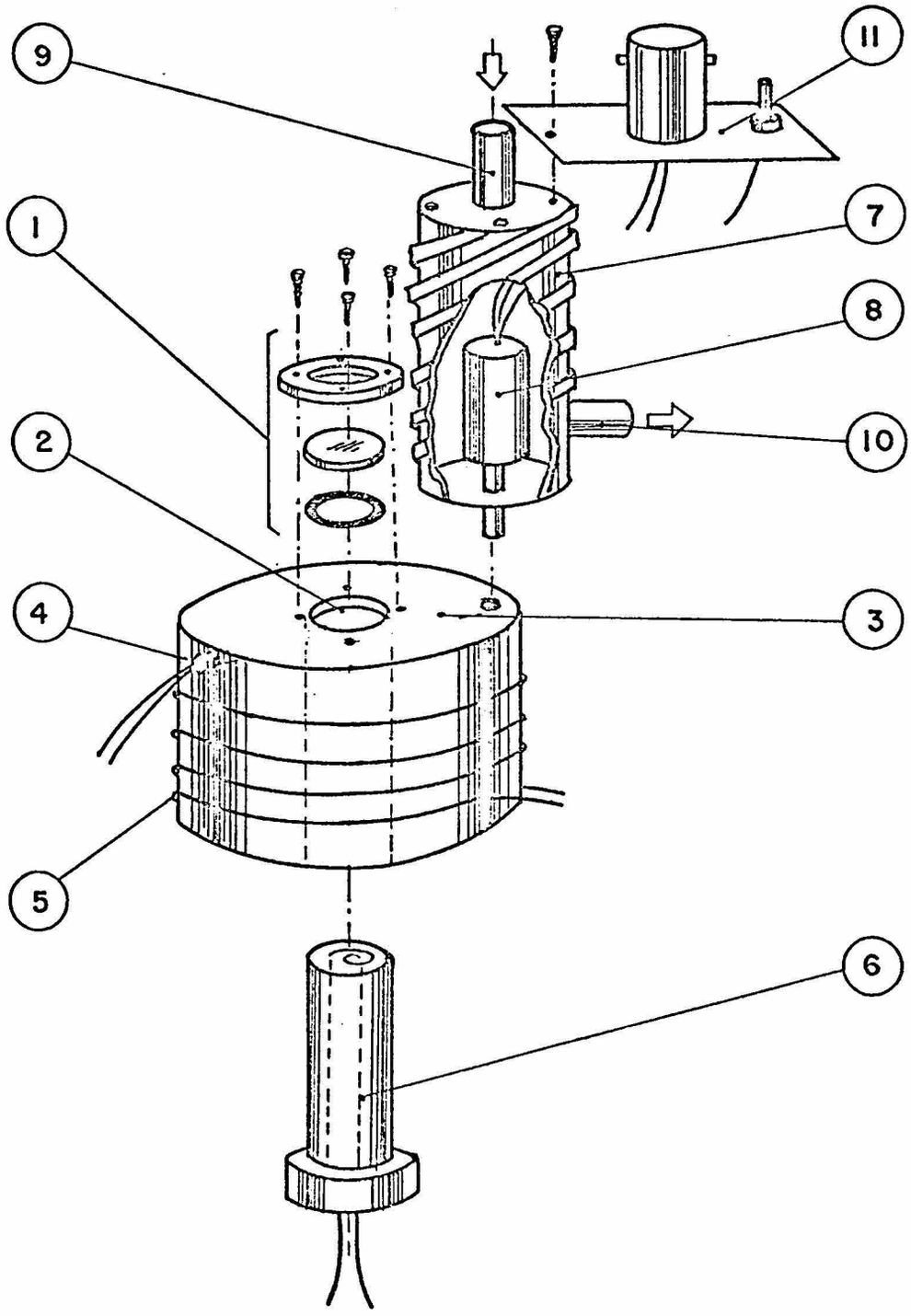

Fig. 4

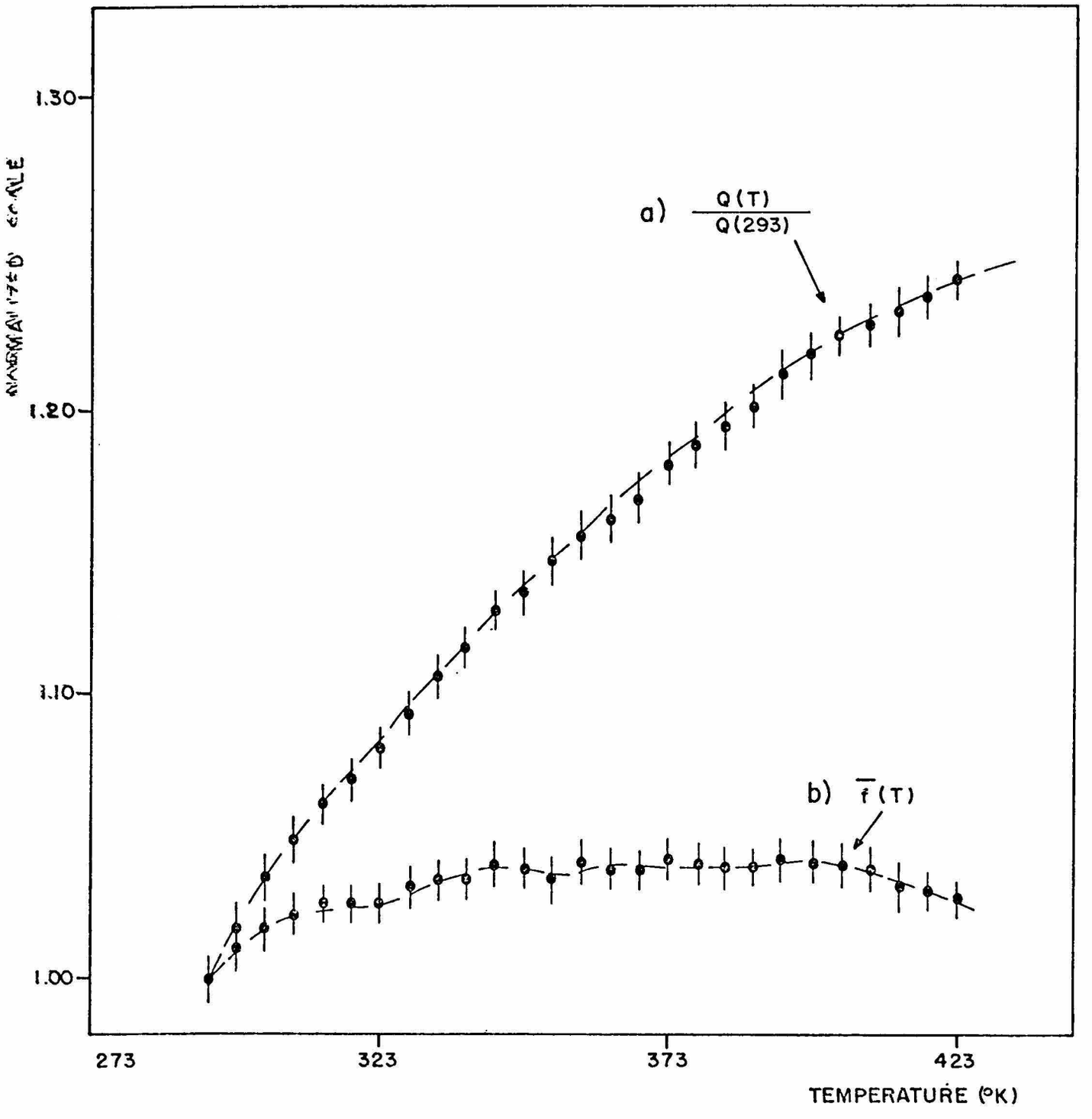

Fig. 5

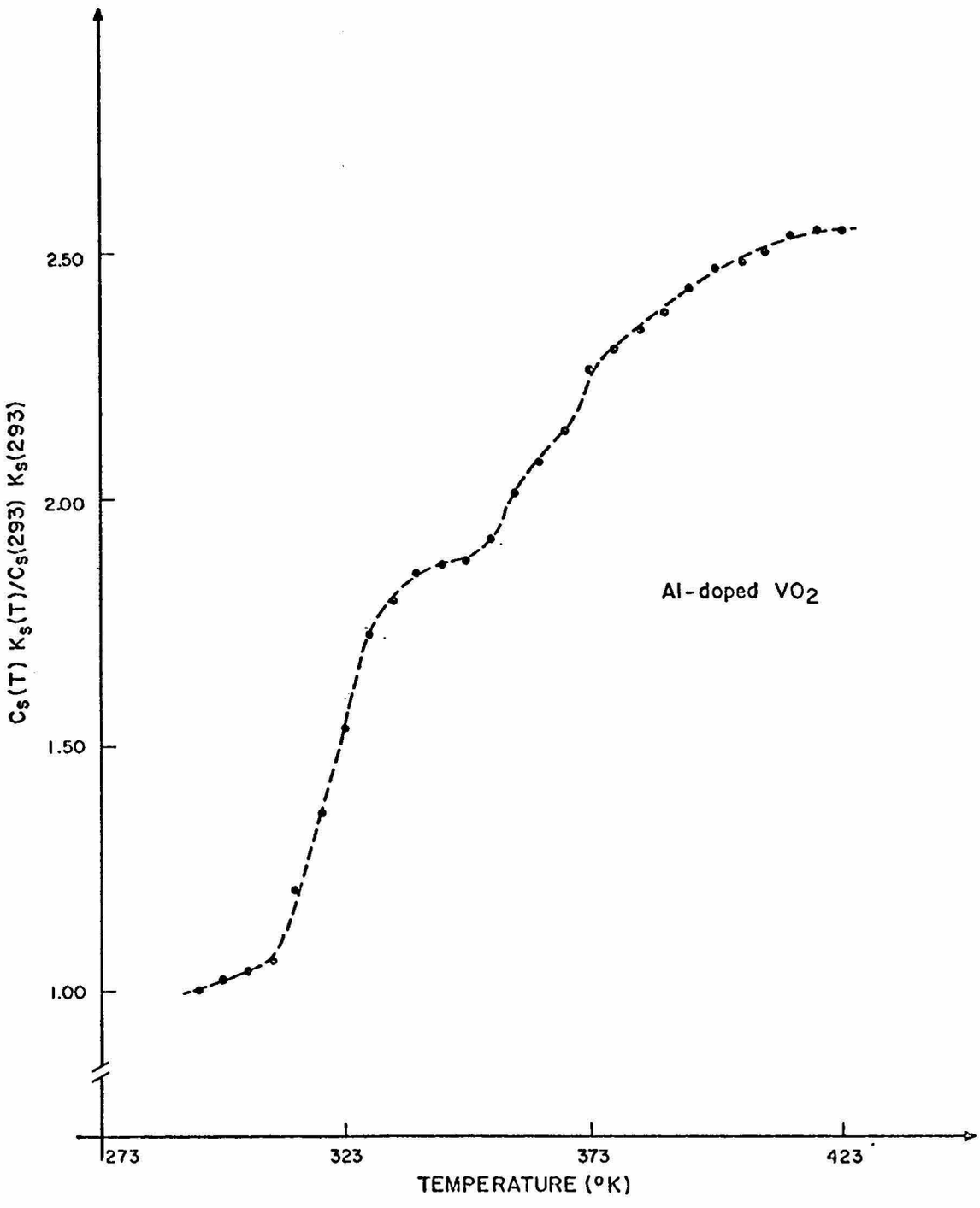
2.50
2.00
1.50
1.00
$C_s(T)\ K_s(T)/C_s(293)\ K_s(293)$
Al-doped VO_2
273
323
373
423
TEMPERATURE (°K)

Fig. 6