$C_{p_1} = \Delta W_1/(T_2 - T_1)$ $(T_1 < T_2 < T_c)$ est plus importante que celle observée lorsque l'on redescend à T_1 soit $C_{p_2} = \Delta W_2/(T_2 - T_1)$ ou celle mesurée lorsque l'on remonte à T_2 : $C_{p_3} = \Delta W_3/(T_2 - T_1)$.

La valeur de C_p obtenue dans les deux derniers cas (et aussi lors des cycles suivants) est toujours identique et peut être appelée chaleur spécifique réversible C_{pR} du matériau pour l'intervalle de température (T_1, T_2). La différence $(C_{p_1} - C_{pR})\,\Delta T$ semble correspondre à une chaleur latente qui n'est pas restituée lors des cycles en raison de l'hystérésis thermique de la transition (environ 10 °C).

Ainsi pour le titanate de plomb (Fig. 2) on peut constater que C_{p_1} atteint 0,1 cal/g °C à la température de transition $T_c = 488$ °C (montée de température) alors que C_{pR} n'excède pas 0,14 cal/g °C. Par contre en dessus de T_c on a $C_{p_1} = C_{pR} = 0,1$ cal/g °C. On peut évaluer

$$L = \int_0^{Tc} (C_{p_1} - C_{pR})\,dT = 360 \text{ cal/mole}$$

qui correspond à la surface S_1 et

$$\Delta H = \int_0^{Tc} \Delta C_p\,dT = 500 \text{ cal/mole}$$

surface $S_1 + S_2$.

ΔC_p représentant l'anomalie totale de C_p par rapport aux valeurs obtenues en dessous de 430 °C dans la phase antiferroélectrique. Ce résultat concorde avec ceux obtenus précédemment [3], [7] au moyen d'appareils d'analyse thermique différentielle.

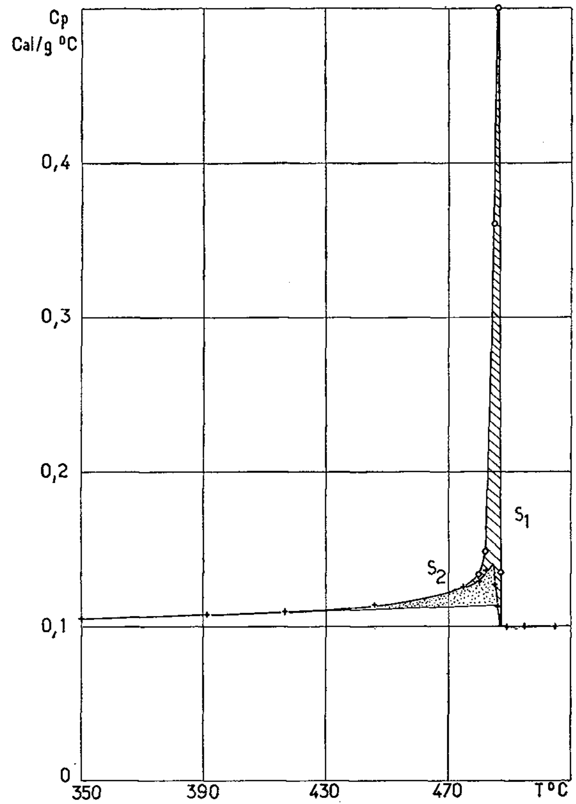

FIG. 2. — Chaleur spécifique de $PbTiO_3$ céramique. Courbe + chaleur spécifique réversible C_{pR}. Courbe 0 chaleur spécifique obtenue à la première montée : S_1 aire associée à L ; $S_1 + S_2$ aire associée à ΔH.

La température de transition en descente de température est $T_c' = 479$ °C et des phénomènes analogues sont observables.

SPECIFIC HEAT ANOMALY IN THE NEIGHBOURHOOD OF A FERRO-PARAELECTRIC TRANSITIONS

Abstract. — We report our measurements of specific heat variations versus temperature in the neighbourhood of ferro-paraelectric transitions. Two typical exemples have been chosen : T. G. S. for second order transition and $PbTiO_3$ for first order transition. The occurrence of a thermal hysteresis in the second case is used to evaluate the latent heat associated with the transition.

It is known that when you raise the temperature through a ferro-paraelectric or an antiferro-paraelectric transition an important endothermic effect can be detected [1], [2]. This effect, which becomes exothermic when you lower temperatures, spreads over a range which can vary from a few degrees to several tens of degrees according to the nature of the material under study. Contributing to this phenomenon among others are : the thermal effect which goes together with the off-set or the on-set of spontaneous polarization ; the one resulting from contraction or dilatation of the unit cell ; the one resulting form the appearance or the disappearance of a domain structure etc... [3], [4].

One of the most important problems which still remains to be solved concerning these transitions is to know if, from a thermodynamic point of view, they can be considered as being of the first or the second order. In other words : is the above-said thermal effect only due to a gradual change in the specific heat, or is there a latent heat associated with these transitions ? The answer to that question would be easy to find if the material under study were monocrystals with a well known transition temperature : for instance for T. G. S. crystals there is a regular rise of the specific heat under $T_c = 49$ °C and an abrupt fall of its value can be observed at the Curie-temperature, but no anomalous thermal effect in the neighbourhood of T_c can be detected (Fig. 1). We may therefore conclude that this transition belongs to the second order.

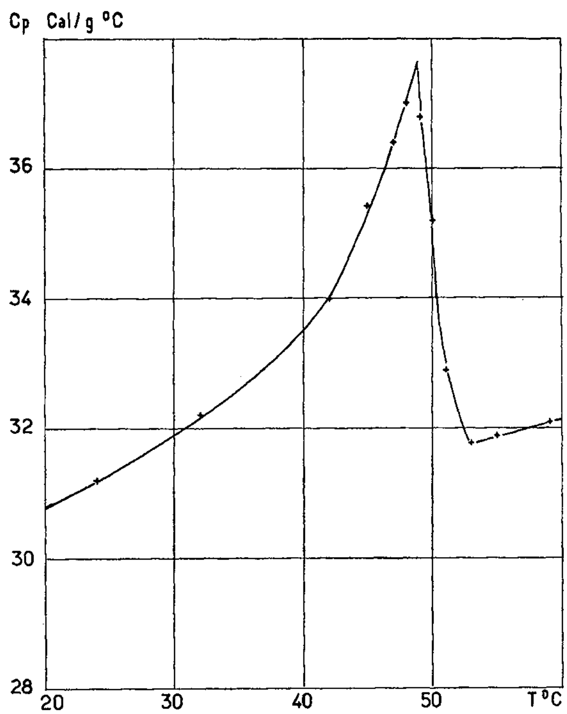

FIG. 1. — Specific heat variation of T. G. S.

On the contrary, when we have to study fritted ceramic samples of lead zirco-titanate there occur internal strains within the samples which spread the transition over several degrees, and then it is very difficult to distinguish a latent heat from a progressive change of the specific heat. However we have been able with the help of an apparatus specially designed for that kind of measurements to contribute a new approach to the study of these phenomena [5], [6].

This apparatus enabled us to put a sample through loops of temperatures neighbouring T_c, and to measure $C_p = \Delta W/\Delta T$ corresponding to increases or decreases in temperature of $T = 1$ to 2 °C. We could then observe that when you raise the temperature for the first time from T_1 to T_2 (in the neighbourhood of T_c) the specific heat measured $C_p = W_2/(T_2 - T_1)$ is more important than the one observed when you lower the temperature from T_2 to T_1, or than the one observed when you rise again from T_1 to T_2.

The value of C_p measured in the course of the last two experiments, which is found to be the same, can be called reversible and can be considered as the true specific heat (C_{pR}).

The difference $(C_{p_1} - C_{pR})\,\Delta T$ is likely to correspond to a latent heat which did not appear in the course of the later experiments because of the thermal hysteresis of these transitions. In some cases that hysteresis can reach up to ten degrees C.

For instance in the case of $PbTiO_3$ (Fig. 2) we have :

$T_c = 488$ °C when you raise the temperature ;
$T_c' = 479$ °C when you lower it ;
$C_{p_1} \# 0,5$ cal/g °C between 486 and 488 °C ;
$C_{pR} \# 0,14$ cal/g °C for the same range of temperature ;
$C_{p_1} = C_{pR} \# 0,1$ cal/g °C just above T_c.

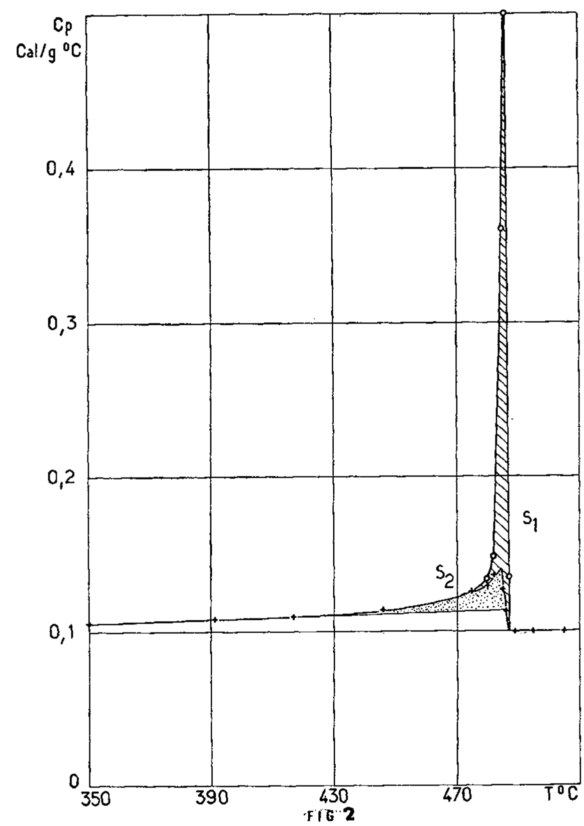

FIG. 2. — Specific heat variation of $PbTiO_3$. Curve + : reversible part of $C_p = C_{pR}$. Curve 0 : value of C_p measured during the first raising of temperature : S_1 area associated with « l » ; $S_1 + S_2$ area associated with « ΔH ».

We can also evaluate

$$l = \int_0^{T_c} (C_{p_1} - C_{pR})\, dT = 360 \text{ cal/mole}$$

whereas before now we could only know the whole thermal effect [3], [7]

$$\Delta H = \int_0^{T_c} \Delta C_p \, dT \neq \neq 500 \text{ cal/mole}$$

in which formula ΔC_p stands for the specific heat anomaly.

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