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Abstract. The specific heat capacities of La$_x$Pr$_{1-x}$P$_5$O$_{14}$ crystals with $x = 0.9$ and 0.7 were measured with a differential scanning calorimeter over the temperature range 350–450 K. A jump in the specific heat capacity at the phase transition temperature of 402 K and one thermal anomaly at about 385 K were found within experimental error. Factors contributing to the specific heat capacities were considered.

Since the 1970s the lanthanide pentaphosphates MP$_5$O$_{14}$ (M $\equiv$ La to Tb) have been widely studied because of their promising properties as efficient laser materials and the occurrence of ferroelastic phase transitions. The crystallographic measurements have shown that the space groups are from monoclinic P2$_1$/c or C2/c to orthorhombic Pcmn or Pncm when the phase transitions occur with no modification of the number of atoms in the unit cell (Schulz *et al* 1974). The ferroelastic behaviours of MP$_5$O$_{14}$ (M $\equiv$ La to Tb) have been examined using optical methods, especially the softening of one acoustic and two optical modes through light scattering techniques (Toledano *et al* 1976, Fox *et al* 1976, Weber *et al* 1975, Budin *et al* 1975). Loiacono *et al* (1978) first measured the specific heat capacities of NdP$_5$O$_{14}$ and PrP$_5$O$_{14}$ near the ferroelastic phase transitions and observed one thermal anomaly approximately 20 K below T_c. Barthou and Blanzat *et al* (1981) identified that, near room temperature, another thermal anomaly was clearly observed. Both of these groups of workers did not give convincing explanations of their differential scanning calorimetry (DSC) results. In this paper a study of the specific heat capacities of La$_x$Pr$_{1-x}$P$_5$O$_{14}$ crystals using the DSC method over the temperature range 350–450 K is presented and we observed one thermal anomaly at about 385 K within experimental error. A possible interpretation of these results is presented.

Two high-quality single crystals of La$_x$Pr$_{1-x}$P$_5$O$_{14}$ with $x = 0.9$ and 0.7 were grown from phosphoric acid solution using the detailed procedures described by Tofield *et al* (1974).

The specific heat capacity data were obtained with a Perkin–Elmer model DSC-2 differential scanning calorimeter at a scanning rate of 5 K min^{-1} with a sensitivity of 4.18×10^{-3} J s^{-1} (1 mcal s^{-1}). We used a specimen having a mass of about 30×10^{-3} g. So we obtain that the inaccuracy associated with the specific heat capacity measurement is less than 1.25×10^{-3} J g^{-1} K^{-1}. The temperature was calibrated with an experimental error of less than 2 K. The temperature range was 350–450 K for our heating and cooling procedures. The experimental data were analysed by a computer and plotted as a diagram.

Table 1. The measured specific heat capacity.

Sample	Mass (g)	Temperature (K)	C_p ($J\,g^{-1}\,K^{-1}$)	Jump in C_p ($J\,g^{-1}\,K^{-1}$)
$La_{0.7}Pr_{0.3}P_5O_{14}$	35×10^{-3}	350.0–380.0	$3.010 \times 10^{-1} + 9.823 \times 10^{-4}\,T$	
$La_{0.7}Pr_{0.3}P_5O_{14}$	35×10^{-3}	384.8–403.2	$1.881 \times 10^{-1} + 1.254 \times 10^{-3}\,T$	3.344×10^{-3}
$La_{0.7}Pr_{0.3}P_5O_{14}$	35×10^{-3}	406.4–450.0	$3.595 \times 10^{-1} + 7.775 \times 10^{-4}\,T$	1.839×10^{-2}
$La_{0.9}Pr_{0.1}P_5O_{14}$	38×10^{-3}	350.0–376.0	$3.595 \times 10^{-1} + 8.193 \times 10^{-4}\,T$	
$La_{0.9}Pr_{0.1}P_5O_{14}$	38×10^{-3}	380.0–402.0	$3.511 \times 10^{-1} + 8.276 \times 10^{-4}\,T$	2.508×10^{-3}
$La_{0.9}Pr_{0.1}P_5O_{14}$	38×10^{-3}	410.0–450.0	$4.514 \times 10^{-1} + 6.7425 \times 10^{-4}\,T$	1.505×10^{-2}

On performing this experiment it was found that the specific heat capacity decreased suddenly with a precision of ± 0.5 K at the phase transition temperature of 402 K. On measuring through heating and cooling steps, no hysteresis was observed. We infer that the phase transition was of second-order ferroelastic type. From the experimental results shown in table 1 we find that the jumps in the specific heat capacity at about 385 K and 402 K are within experimental accuracy. We also found that the rates of change in the specific heat capacity with temperature are different in the three temperature ranges: 350–385 K, 385–402 K and 402–450 K. We therefore concluded that the jumps in the specific heat capacities at 385 K and 402 K are related to the thermal anomaly and the ferroelastic phase transition, respectively. Figure 1 shows the experimental results of the specific heat capacities measured for two samples, and the anomaly is denoted with an arrow.

Previous work on LaP_5O_{14} and PrP_5O_{14} has shown that the ferroelastic phase transition was from $P2_1/c$ (the low-temperature phase) to $Pnca$ (high-temperature phase). In fact the lanthanide pentaphosphates are isostructural and the rare-earth atoms are linked along the crystallographic c axis with M–O–P–O–M bands. Tadashi *et al* (1976) have concluded that the phase transition temperature was likely to increase with decrease in the radius of the lanthanide ion. Our results, as shown in table 1, indicate that the temperature of the phase transition of $La_{0.7}Pr_{0.3}P_5O_{14}$ is greater than that of $La_{0.9}Pr_{0.1}P_5O_{14}$ which is consistent with the above remarks. These compounds show similar physical properties.

Despite its jump at the transition point and at about 385 K, the specific heat capacity was observed to undergo a slight increase with increasing temperature in the temperature range 350–450 K. In our opinion this result can be explained as due to the contributions of three physical factors. The first is a domain effect which will be discussed in detail below. The second may be associated with the Debye model, which indicates that within a small temperature range around the Debye temperature T_D (which we assume to be 600 K) the specific heat capacity is approximately linear and increases slightly with increasing temperature just as shown by figure 2, curve B. Because the phonon states at a finite temperature are not fully occupied, higher temperatures correspond to when more high-energy states are occupied, which gives a greater contribution to the specific heat capacity. The third effect is attributed to the phenomenological model presented by Errandonea (1980). From the Landau free energy of this model we obtain the following results for the specific heat capacity:

$$C_p = T\alpha^2/2\beta' \qquad T < T_c \qquad (1)$$

$$\Delta C_p = T_c\alpha^2/2\beta' \qquad T = T_c \qquad (2)$$

$$C_p = 0 \qquad T > T_c \qquad (3)$$

where the parameters α and β' are constants and were defined by Errandonea.
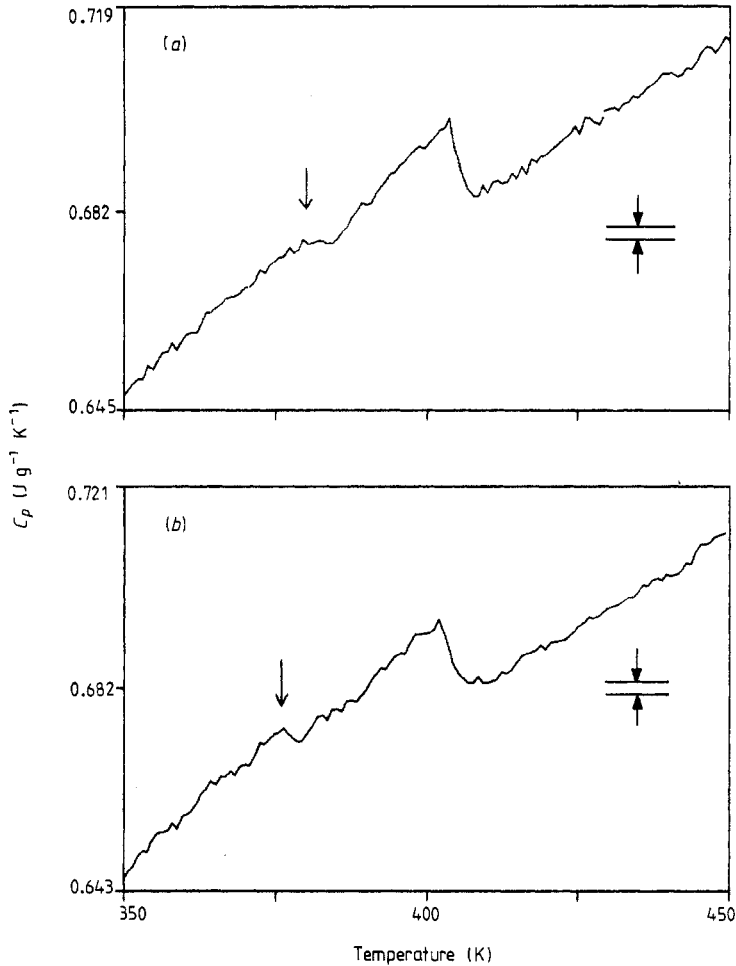
Figure 1. The specific heat capacity curves of (*a*) $La_{0.7}Pr_{0.3}P_5O_{14}$ and (*b*) $La_{0.9}Pr_{0.1}P_5O_{14}$ single crystals. The anomaly at about 380 K is denoted with an arrow. The experimental inaccuracy is indicated on the right-hand side of the figure.

The displacive structure phase transition from the monoclinic to the orthorhombic phase, or the ferroelastic transition, contributes mainly to the jump in the specific heat capacity at the transition temperature. As the temperature approaches T_c, the structural change perturbs the interactions between atoms. It may be assumed that this change will add to the crystal–lattice non-harmonic interactions and consequently affect the phonon state density. In fact, from the thermodynamic point of view these effects arise from one term in the Landau free energy, the coupling term between the order parameter and the thermally induced strain components. On the basis of the Landau free energy, two possible phases may exist. When the second-order ferroelastic transition occurs, a jump in the specific heat capacity at the transition temperature may be observed.

Using equations (1)–(3) we analyse the structural contribution to the specific heat capacity. In the monoclinic phase the specific heat capacity shows a slight linear increase with increasing temperature as given by equation (1). In the orthorhombic phase, however, the structural contribution is zero, as given by equation (3). This result corresponds to a simplification of the assumptions in Errandonea's model in which the
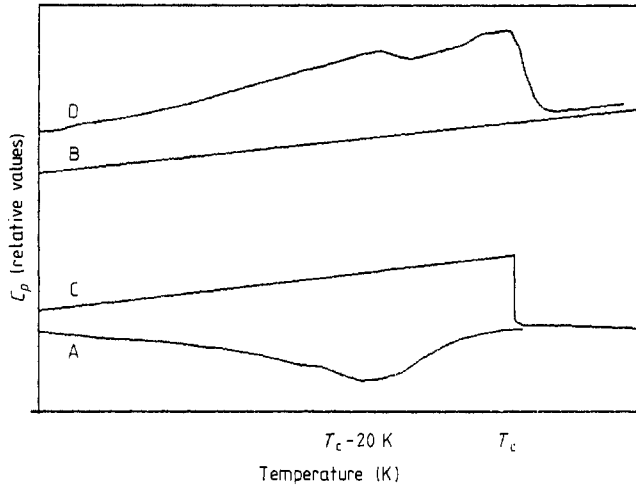
Figure 2. The specific heat capacity curves calculated using a phenomenological model: curve A, domain contribution; curve B, Debye contribution; curve C, phase transition contribution; curve D, total result.

thermal expansion of the orthorhombic phase is neglected. At the transition temperature the specific heat capacity becomes discontinuous and its jump is represented by equation (2). These three structural contributions are shown by figure 2, curve C. In our experiment the jump in the specific heat capacity was about 1.672×10^{-2} J g^{-1} K^{-1} which is similar to the results in previous work. The experimental result of Loiacono *et al* (1978) is 2.215×10^{-2} J g^{-1} K^{-1}. Errandonea estimated that the jump was about 1.756×10^{-2} J g^{-1} K^{-1} using his values for the quantities α and β'.

However, in addition to the major specific heat jump at the phase transition temperature, one anomaly was observed at a temperature of 185 K, about 20 K below T_c. We assume that this is induced by the domains. It is well known that for a displacive ferroelastic phase transition crystal at a temperature below T_c the distortional elastic energy, or the deformation energy y, induced by the internal strain should be considered as an additional contribution to the Landau free energy. However, when the internal strain induces distortion, domains will appear. This will decrease the distortional elastic energy until the two factors balance. We assume that the influence of the domains on the specific heat capacity is negative. We assume that the domain wall density increases with increasing temperature and that it is approximately proportional to $(T_c - T)^{-1}$ up to the transition (Wang *et al* 1987). Surprisingly, the domain wall contribution to the internal friction is not so simple. Wang *et al* observed that at about 398 K (T_c is 414 K for the sample NdLaP$_5$O$_{14}$) there existed an internal friction peak P$_2$ (16 K below T_c) which was attributed to the effect of the domain wall motion. We suggest that the domain wall contribution to the specific heat capacity is somewhat similar. With the temperature approaching T_c from below, the domains contribute negatively to the specific heat capacity and this effect eventually reaches its maximum at about 20 K below T_c. In the temperature range from $T_c - 20$ K to T_c this effect becomes less until the phase transition occurs. The above domain wall effects are shown by figure 2, curve A. The domain wall effect is less than that induced by the phase transition.

In summary, the total free energy has three parts: the Debye model, the Landau free energy and the distortional energy associated with the domains. As regards the magnitudes of these contributions to the specific heat capacity, the largest is due to the

Debye model, then the Landau part and finally the domain-induced part. Other factors which may contribute to the free energy are ignored in this simple model. The three contributions that we have considered are shown in figure 2. Curves B, C and A represent the Debye model, the Landau free energy and the domain-induced contributions respectively, to the specific heat capacity. Curve D, corresponding to the sum of the above three factors, is similar to the experimental DSC curves in figure 1. The phenomenological model is thus consistent with our experimental results.

In conclusion, two specific heat capacity jumps were found: the first corresponds to the domain-induced effect, and the second to the ferroelastic phase transition. The linear increase in specific heat capacity with increasing temperature can be described using a simple phenomenological model.

Acknowledgment

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