

Materials for Devices: Problem Set 2

5. Consider a ferroelectric material subject to an applied electric field of magnitude E . The free energy of the system is given by:

$$\mathcal{F}(P, T) = a(T - T_c)P^2 + \frac{b}{2}P^4 - EP,$$

where P is the polarisation, T the temperature, and a , b , and T_c are positive scalar parameters.

- (i) Find the minimisation condition for the free energy with respect to the polarisation. Hence, argue that $P = 0$ is not a possible state for the system.
- (ii) Calculate the zero-field electric susceptibility of the system:

$$\chi = \frac{1}{\varepsilon_0} \left. \frac{\partial P}{\partial E} \right|_{E=0}.$$

- (iii) Sketch χ as a function of temperature and discuss what happens near T_c .

Solution

- (i) The extrema of a function are given by the points at which its first derivative vanishes. In our case, the derivative of the free energy with respect to polarisation is:

$$\frac{\partial \mathcal{F}}{\partial P} = \frac{\partial}{\partial P} \left(a(T - T_c)P^2 + \frac{b}{2}P^4 - EP \right) = 2a(T - T_c)P + 2bP^3 - E.$$

Therefore, the condition for extrema of the free energy with respect to polarisation is:

$$2a(T - T_c)P + 2bP^3 - E = 0. \tag{1}$$

In this equation, $P = 0$ is not a solution for $E \neq 0$. This implies that under an applied field, the polarisation is non-zero at all temperatures.

- (ii) The electric susceptibility relates the polarisation to the applied field according to $\mathbf{P} = \varepsilon_0 \chi \mathbf{E}$. From this expression, we can write the zero-field electric susceptibility as:

$$\chi = \frac{1}{\varepsilon_0} \left. \frac{\partial P}{\partial E} \right|_{E=0}.$$

The expression in Eq. (1) gives a condition for the polarisation under an applied field. Differentiating the full expression with respect to E yields:

$$\begin{aligned} \frac{\partial}{\partial E} (2a(T - T_c)P + 2bP^3 - E) &= 0 \\ 2a(T - T_c) \frac{\partial P}{\partial E} + 6bP^2 \frac{\partial P}{\partial E} - 1 &= 0 \\ [2a(T - T_c) + 6bP^2] \frac{\partial P}{\partial E} - 1 &= 0 \end{aligned}$$

Re-arranging, we obtain:

$$\frac{\partial P}{\partial E} = \frac{1}{2a(T - T_c) + 6bP^2}$$

Remembering the results from Problem 4, we have two possibilities in the limit $E \rightarrow 0$:

(a) $T > T_c$, for which $P = 0$. In this case, we get:

$$\left. \frac{\partial P}{\partial E} \right|_{E=0} = \frac{1}{2a(T - T_c)}.$$

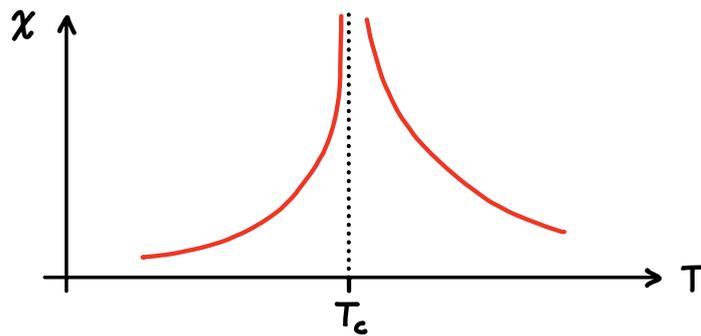
(b) $T < T_c$, for which $P = \pm \sqrt{-\frac{a}{b}(T - T_c)}$. In this case, we get:

$$\begin{aligned} \left. \frac{\partial P}{\partial E} \right|_{E=0} &= \frac{1}{2a(T - T_c) + 6b \left(\pm \sqrt{-\frac{a}{b}(T - T_c)} \right)^2} \\ &= \frac{1}{2a(T - T_c) + 6b \left(-\frac{a}{b}(T - T_c) \right)} \\ &= \frac{1}{2a(T - T_c) - 6a(T - T_c)} \\ &= -\frac{1}{4a(T - T_c)} \end{aligned}$$

Overall, the zero-field susceptibility is:

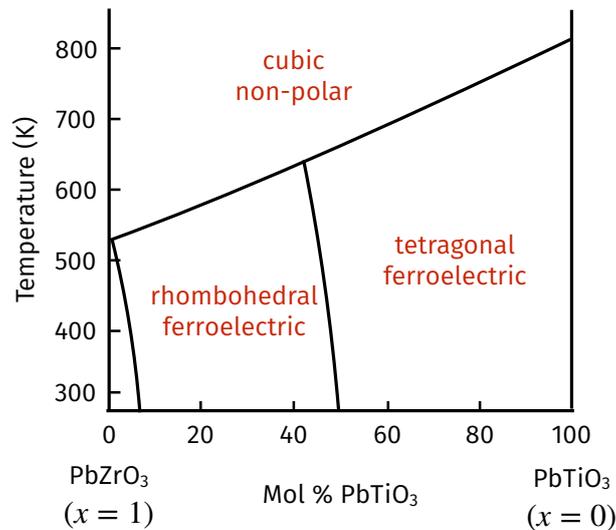
$$\chi = \begin{cases} \frac{1}{2a\varepsilon_0(T - T_c)} & \text{for } T > T_c, \\ -\frac{1}{4a\varepsilon_0(T - T_c)} & \text{for } T < T_c. \end{cases}$$

(iii) The Figure below depicts χ as a function of temperature. There is a divergence of the susceptibility at the phase transition temperature $T = T_c$, indicating that near a phase transition the material can very easily polarise even with a very small external field.



6. Consider the phase diagram of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ shown in the Figure below.

- (i) What is the Curie temperature of $\text{PbTi}_{0.4}\text{Zr}_{0.6}\text{O}_3$?
- (ii) What is the crystal structure of $\text{PbTi}_{0.4}\text{Zr}_{0.6}\text{O}_3$ at room temperature? And the crystal structure of $\text{PbTi}_{0.6}\text{Zr}_{0.4}\text{O}_3$ at room temperature?
- (iii) What conditions of polarisation would result in a specimen of $\text{PbTi}_{0.6}\text{Zr}_{0.4}\text{O}_3$ after each of the following treatments:
 - (a) Strong electric field applied at 750 K, held for some hours, then switched off. Specimen cooled to 300 K.
 - (b) Strong electric field applied at 620 K, held for some hours, cooled to 300 K, then field switched off.



Solution

- (i) From the diagram, the Curie temperature of $\text{PbTi}_{0.4}\text{Zr}_{0.6}\text{O}_3$, corresponding to $x = 0.6$ and to a 40% molar percentage of PbTiO_3 , is about 640 K.
- (ii) At room temperature, $T = 300$ K, $\text{PbTi}_{0.4}\text{Zr}_{0.6}\text{O}_3$ ($x = 0.6$, 40% molar percentage of PbTiO_3) adopts a rhombohedral crystal structure and $\text{PbTi}_{0.6}\text{Zr}_{0.4}\text{O}_3$ ($x = 0.4$, 60% molar percentage of PbTiO_3) adopts a tetragonal crystal structure.
- (iii) (a) $\text{PbTi}_{0.6}\text{Zr}_{0.4}\text{O}_3$ corresponds to $x = 0.4$ and 60% molar percentage of PbTiO_3 , and at a temperature of 750 K the system is in the cubic non-polar phase. The applied field polarises the sample, but when the field is switched off the polarisation vanishes. Upon cooling the specimen to 300 K, there will be no net polarisation due to the presence of polarisation domains pointing in different directions.
- (b) At a temperature of 620 K, the system is in the tetragonal polar phase. Upon the application of an electric field, the sample becomes polarised along the allowed crystallographic direction most aligned with the applied field. After cooling and switching off the applied field, the sample retains its polarisation as it is in the ferroelectric phase.

7. Consider the following data for iron and its ions:

Species	Net magnetic moment ($\times 10^{-23} \text{ Am}^2$)
Fe atom	2.06
Fe ²⁺ cation	3.71
Fe ³⁺ cation	4.64

- (i) Calculate the saturation magnetisation of elemental α -iron in the bcc structure.
(ii) Calculate the saturation magnetisation of magnetite whose cubic cell has lattice parameter $a = 8.39 \text{ \AA}$.

Solution

- (i) The bcc structure of α -iron has a single atom in the primitive cell. The conventional cubic cell has a lattice parameter of 2.87 \AA and two atoms per cell. The magnitude of the saturation magnetisation in SI units is given by:

$$M_{\text{saturation}} = \frac{\text{magnetisation per atom}}{\text{volume per atom}} = \frac{2.06 \times 10^{-23}}{\frac{1}{2} \times (2.87 \times 10^{-10})^3} = 1.74 \times 10^6 \text{ Am}^{-1}.$$

- (ii) Magnetite is a ferrimagnetic material whose magnetisation is due to the Fe²⁺ ions in octahedral sites. There are 8 such ions, giving a total magnetisation in SI units of:

$$M_{\text{saturation}} = \frac{\text{magnetisation per atom}}{\text{volume per atom}} = \frac{3.71 \times 10^{-23}}{\frac{1}{8} \times (8.39 \times 10^{-10})^3} = 5.03 \times 10^5 \text{ Am}^{-1}.$$

8. A cubic transformer core is made from a nickel-iron-molybdenum ferromagnetic alloy, called supermalloy. Its power dissipation is found to be 2 W at 50 Hz. What is the energy required to switch the magnetisation direction of the transformer core?

Solution

The transformer core undergoes 50 complete cycles (back-and-forth switch) in one second. Therefore, there are a total of 100 magnetisation switches over one second, which means that the energy dissipated per switch in SI units is equal to:

$$\frac{2}{100} = 0.02 \text{ J.} \quad (2)$$