# Effect of thermal filling of trapping centers on the stability of structural phases in semiconductors

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The effect of a thermally induced change in the population of attachment levels (trapping centers) on phase transitions is analyzed. The thermal filling of trapping centers may give rise to a complex sequence of phase transitions. It may also give rise to a temperature interval in which there is an unstable state which is a boundary region between phases. This behavior is most likely to be observed in the course of incommensurate–commensurate phase transitions near the Lifshitz point.

The properties of structural phase transitions in semiconductors are largely determined by the mutual effects of the electron and lattice subsystems. There are accordingly changes in the energy intervals of the electron spectrum upon a phase transition, and there is a shift of the phase transition temperature upon changes in the populations of trapping centers.[1] These properties of a system are manifested experimentally in several unusual phenomena: self-oscillations of an order parameter,[2,3] a photostimulated appearance of an incommensurate phase,[4,5] and a stimulating effect of a rapid temperature variation on structural changes.[6,7] The latter phenomenon has been linked with the dynamics of the filling of trapping centers upon a rapid change in temperature.[7] In the present letter we are reporting a study of how a temperature-induced change in the population of attachment levels (trapping centers) affects phase transitions in the course of a slow, quasistatic change in temperature.

As the temperature is lowered, there is a progressive filling of attachment levels. The effective temperature interval in which the trapping centers are filled is 10–40 K. Features can appear in the structural properties of the system in this temperature interval. This behavior is most likely if the temperature interval of interest is near the temperatures of phase transitions, especially if polycritical points are nearby.[4] Such a case is the subject of the present study.

We consider a ferroelectric semiconductor near a phase transition. The effect of the electron subsystem on the phase transition is manifested in a shift of the transition temperature $T_p$ (Ref. 1):

$$T_p = T_c - \frac{am}{a}, \tag{1}$$

where $T_c$ is the transition temperature in the absence of the electron subsystem, $\alpha' = 2\pi/C$ ($C$ is the Curie–Weiss constant), $a$ is a coefficient in the expansion of the electron energy in the trapping centers in powers of the order parameter, and $m$ is the density of electrons at attachment levels. In addition, for phase transitions to an

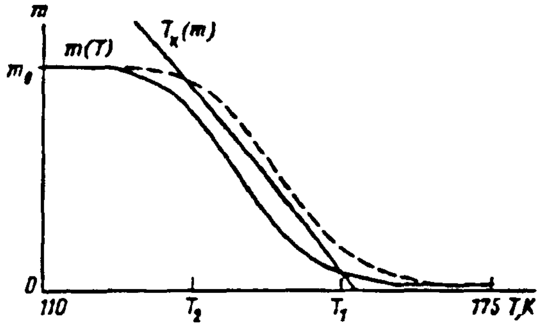

FIG. 1. Plots of the electron density versus the temperature, $m(T)$, and of the phase-transition temperature versus the electron density in the attachment levels, $T_k(m)$. Dashed curve—Temperature dependence of the electron density, $m(T)$, in the commensurate phase; solid line—the same, in the incommensurate phase.

incommensurate phase there is another, nonlinear shift of the temperatures of the phase transition, $T_i$ and $T_k$, which results from the proximity to the Lifshitz point. In other words, there is a renormalization of the coefficient $\delta$ $(\delta_m=\delta+cm)$ in front of the term $(\partial\eta/\partial x)^2$ (Ref. 5):

$$T_i=T_{i0}+\frac{1}{\alpha'}\left(\frac{2\delta cm+c^2m^2}{2\sigma}-am\right), \tag{2}$$

$$T_k=T_{k0}-\frac{1}{\alpha'}\left(2.2\frac{2\delta cm+c^2m^2}{\sigma}+am\right). \tag{3}$$

Here $T_{i0}$ and $T_{k0}$ are the temperatures of the paraelectric-phase–incommensurate-phase and incommensurate-phase–commensurate-phase transitions, respectively, in the absence of the electron subsystem.

The steady-state electron density at attachment levels is[3]

$$m(T)=\frac{n_0M}{n_0+N_c\exp\left[-(u_0+\tilde{a}\eta^2)/kT\right]}. \tag{4}$$

Here $n_0$ is the density of conduction electrons, $M$ is the density of attachment levels, $N_c$ is the density of states in the conduction band, and $u=u_0+\tilde{a}\eta^2$ is the energy interval from the bottom of the conduction band to the attachment levels, which depends on the order parameter $\eta$ (Ref. 3). The steady-state electron density in attachment levels, $m(T)$, in the high-temperature phase differs from that in the low-temperature phase because in the latter phase there is a jump of $\Delta$ $(\Delta=\tilde{a}\eta^2)$ in the energy interval $u$.

Figures 1 and 2 show the temperature dependence of the electron density $m(T)$.

For definiteness we will discuss below the case of a first-order phase transition from an incommensurate phase to a commensurate phase. The temperature of this phase transition, $T_k$, is greatly altered by electrons in attachment levels [see (3)].

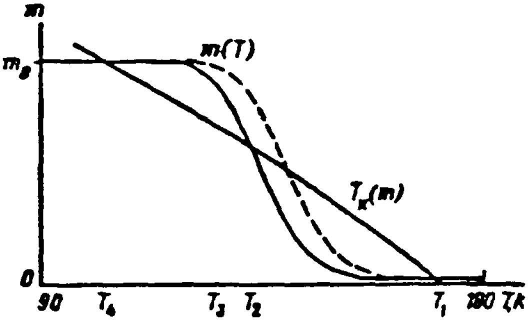

FIG. 2. The same as in Fig. 1, for other values of the constants $a$ and $c$.

The intersection of the curve of $m(T)$ in (4) with the curve of $T_k(m)$ from (3) (the phase-transition temperature as a function of the density of electrons in attachment levels) gives us the temperature of the phase transition in a real crystal (Figs. 1 and 2). To the right of the $T_k(m)$ curve we are in the incommensurate phase; to the left we are in the commensurate phase. When the effective filling of trapping centers occurs near the phase-transition temperature $T_k$, the following cases are possible:

1) First, there is the case in which the filling of trapping centers occurs in either the incommensurate or the commensurate phase. New phases do not arise in this case, and all that is possible is a change in the behavior of the low-temperature phase. We will come back to this point a bit further on (Fig. 3).

2) Figure 1 shows the case in which the filling of trapping centers occurs in the immediate vicinity of a first-order incommensurate–commensurate phase transition. As the temperature is lowered, after the phase transition at $T_1$, there is an abrupt change in the width of the energy interval, $u=u_0+\Delta$. This abrupt change leads to a decrease in the probability for a thermal emptying of trapping centers into the conduction band. As a result, trapping centers are filled to a level $\sim M$; as a further result, the effective phase-transition temperature becomes $\sim T_2$, and the system is in the incommensurate phase. Now the steady-state value of the density of electrons at attachment levels, $m$, is much smaller than $M$. Correspondingly, the effective transition temperature is $\sim T_1$, and we have come back to the incommensurate phase and

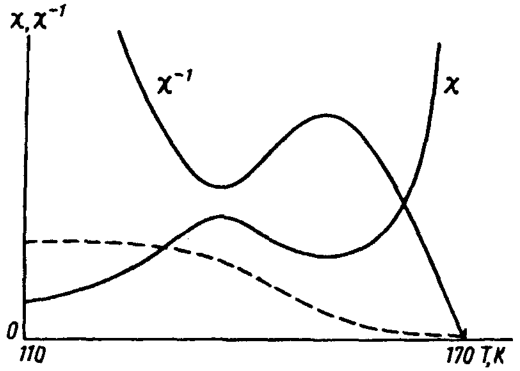

FIG. 3. Temperature dependence of the susceptibility, $\chi(T)$, and of its reciprocal, $\chi^{-1}(T)$, in the temperature region in which the trapping centers are filled, $m(T)$ (the dashed curve).

to the starting point of our dynamics. As a result of this dynamics, the density of electrons at attachment levels varies along the $T_k(m)$ curve as the temperature is changed from $T_1$ to $T_2$, while the lattice subsystem is in an intermediate state between incommensurate and commensurate phases. In the temperature interval between $T_2$ and $T_1$, the state of the system is thus unstable, and an arbitrary small perturbation will push the system into one phase or the other.

3) Figure 2 show the case in which the filling of trapping centers occurs in the low-temperature phase in the immediate vicinity of the phase transition. There is also a strong effect of the electron subsystem on the phase transition. As a result, the following sequence of phase transitions occurs as the temperature is lowered. At $T_1$, there is a phase transition from the incommensurate phase to the commensurate phase. At $T_2$, there is a transition from the incommensurate phase to the unstable state whose properties are described in the preceding paragraph. At $T_3$, there is a phase transition from the unstable state to the incommensurate phase, which exists up to $T_4$. At $T_4$, the commensurate low-temperature phase reappears.

In the region of the unstable state, the following is the most likely scenario for the course of events: As soon as the system goes into one of the states, there is a sharp change in the behavior of the density of electrons in attachment levels, $m$. If the density $m$ had previously been increasing, it now begins to decrease, and vice versa. The system remains in the phase which has formed again until the electron density $m$ changes by an amount $\Delta m$, which corresponds to the thermal hysteresis of the phase transition, $\Delta T_h$:

$$\Delta m \approx \frac{\alpha' \Delta T_h}{a + (4.4\delta c/\sigma)} . \tag{5}$$

The inverse phase transition then occurs, and the scenario plays out again. In the unstable state, the electron density $m$ thus lies near the $T_k(m)$ curve in the interval $\Delta m$, and the system goes alternately into one phase and the other.

In addition to the scenario outlined above, there can be a stratification of the system in the unstable state into domains with different phases. However, the state of the system within an individual domain will again be unstable.

Corresponding changes can occur in the course of any other first- or second-order phase transition. An unstable state can arise only in the case of a first-order phase transition. In addition, the state of the ordered phase itself depends on the state of the electron subsystem. Accordingly, if the effective filling of trapping centers occurs in the low-temperature phase, there will be a nontrivial change in the order parameter of the high-temperature phase. This effect will be seen as a feature in the susceptibility:

$$\chi = \left\{ 2\alpha' (T_c - T) - 2 \left( 2.2 \frac{2\delta c m + c^2 m^2}{\sigma} + a m \right) \right\}^{-1}, \quad T < T_k . \tag{6}$$

This behavior may take the form of a diffuse second-order phase transition (Fig. 3).

In summary, we have shown here that the filling of trapping centers can markedly change the order of phase transitions in a system. In addition, in the case of a first-order phase transition, an unstable intermediate state of the system may arise in a certain temperature interval. This behavior is most likely in the vicinity of a phase transition between an incommensurate phase and a commensurate phase.

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