Global dynamic hysteresis in an incommensurate phase in a semiconductor

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A new approach is suggested for describing hysteresis effects in an incommensurate phase. The idea is to take account of the dynamics of the nonuniform electron density in trapping levels in the semiconductor. The interrelation between the observed anomalies in the physical properties of crystals and the characteristics of the semiconducting subsystems is established.

Incommensurate phases have recently attracted much research interest. In a region of an incommensurate phase one observes a thermal hysteresis in physical properties: Physical quantities have different values at a given temperature, depending on whether that temperature was reached by heating or cooling.[1–6] The temperature region in which this difference is observed is comparable to the region in which the incommensurate phase exists, and these phenomena depend strongly on the particular way in which the temperature is varied. This phenomenon is accordingly characterize as a global dynamic hysteresis.[2,5] It has been linked in certain papers[1,7] with a pinning of domain walls at defects or with a redistribution of mobile defects. A problem which remains unresolved is that of evaluating the characteristics of the defects and the extent of their influence. In the present letter we suggest relating the hysteresis phenomena which occur in an incommensurate phase with the dynamics of the electron subsystem in a semiconductor. This is a particularly urgent topic, since experiments have revealed[8] that memory effects in $Sn_2P_2Se_6$ can be altered by the application of light. In view of the relationship between the hysteresis and memory mechanisms,[1] we should thus examine an electron mechanism for hysteresis phenomena in systems like $Sn_2P_2(S_{1-x}Se_x)_6$ and Ag_3AsS_3.

In this letter we consider systems with an arbitrary band gap E_g and a certain density of conduction electrons n_0 ($n_0 \simeq 10^8$–10^{11} cm^{-3}). This density is a phenomenological parameter. In the band gap there are trapping levels, separated from the bottom of the conduction band by an energy interval u, which are involved in a thermal exchange of electrons with the conduction band. The density of trapping levels is denoted by M ($M \simeq 10^{18}$ cm^{-3}), and the density of electrons in these levels is denoted by m. A change in the density m has a strong influence on the parameters of the system near the phase transition. The electric susceptibility $\chi = (\partial^2 G/\partial\eta^2)^{-1}$, for example, depends on the electron density in trapping levels, m (Ref. 9):

$$\chi = \frac{1}{\alpha'(T_i - T) - am} \simeq \chi_0 + a\delta m. \tag{1}$$

Here χ_0 is the susceptibility under equilibrium conditions, and $\delta m = m - m_e$ is the deviation of the density of electrons in trapping levels from the equilibrium value. The

quantity a is determined by the electron-phonon coupling and can be found from the change in the width of the band gap: $E_g = E_{g0} + a\eta^2$ ($a = 10^{-23} - 10^{-18}$ cm^3). The time scales of the relaxation of the electron density in trapping levels to the equilibrium value are fairly long (5–300 min), and the equilibrium values themselves vary with the temperature. In addition, the energy barriers and therefore the electron relaxation times depend on an order parameter. Consequently, in a region of an incommensurate phase a spatially nonuniform density of electrons in trapping levels should arise at equilibrium. The behavior of the period of the order parameter as a function of the temperature will differ from that of the lattice constant. The nonuniform part of the equilibrium density of electrons in trapping levels, which is related to the order parameter, will thus behave in a manner independent of the host lattice. In some particular cell of the crystal, the nonuniform equilibrium density will sometimes increase and sometimes decrease with a change in temperature.

The dynamics of electrons in trapping levels is described by the equation

$$\frac{dm}{dt} = \gamma_n n_0 (M - m) - \gamma_n m N_c \exp\left(-\frac{u_0 + \tilde{a}\eta^2(x)}{kT}\right). \tag{2}$$

Here γ_n is a kinetic coefficient, N_c is the density of states in the conduction band, and $u = u_0 + \tilde{a}\eta^2(x)$ is the energy interval from the bottom of the conduction band to the trapping levels. This interval depends on the order parameter $\eta(x)$, which corresponds to the minimum of the thermodynamic potential. The coefficients of this potential in turn depend on the density of electrons in trapping levels.[10] In the region of an incommensurate phase the order parameter $\eta(x)$ is a periodic function of the coordinate x [in the simplest case, a harmonic function $\eta = \rho \cos(kx)$]. In this case the time scales τ_m of the relaxation of the electrons in the trapping levels are determined by heat-removal processes:

$$\tau_m = (\gamma_n (n_0 + N_c \exp(-u_0/T)))^{-1}. \tag{3}$$

The times τ_m are slow enough for a description of hysteresis with $\gamma_n = 10^{-13}$ cm^3/s^{-1}, $n_0 = 10^8 - 10^{10}$ cm^{-3}, $N_c = 10^{19}$ cm^{-3}, and $u_0/kT = 20$–25 [$u_0 = 0.12$ eV at $T \sim 50$ K in Ag_3AsS_3 (Ref. 9); $u_0 = 0.7$ eV at $T \sim 300$ K in $Sn_2P_2(S_{1-x}Se_x)_6$]. We find $\tau_m = 5$–300 min. From (2) we find the equilibrium density of electrons in trapping levels to be

$$m_e = \frac{n_0 M}{n_0 + N_c \exp\left(-\frac{u_0 + \tilde{a}\eta^2}{kT}\right)}. \tag{4}$$

Expanding m_e in (4) in the small parameter $\tilde{a}\eta^2/kT$, we find the uniform component m_0 and the uniform component $m_1(x)$ of the density of electrons at trapping centers:

$$m_0 = \frac{n_0 M}{n_0 + N_c \exp\left(-\frac{u_0}{kT}\right)}; \quad m_1(x) \approx \frac{N_c \exp\left(-\frac{u_0}{kT}\right) \frac{am_0}{kT}}{n_0 + N_c \exp\left(-\frac{u_0}{kT}\right)} \eta^2(x). \tag{5}$$

The average value of $m_1(x)$ in a sample is on the order of or greater than $0.15m_0$.

As the temperature is lowered, there is a progressive filling of trapping levels. Since the relaxation times are quite long, there is a progressive filling of trapping

levels. Since the relaxation times are quite long, the equilibrium electron density m_0 will be reached only if the cooling is sufficiently slow. If the cooling rate is substantial (0.1–0.001 K/min), essentially no nonuniform electron density $m_1(x)$ will arise in the trapping levels. The reason is that the temperature dependence of an incommensurate wave is not correlated with the temperature dependence of the host lattice. As a result, at any selected point in the lattice at which an electron can localize in a state of a trapping level, the value of the order parameter is constantly changing. Also constantly changing is the increment in the energy barrier associated with the order parameter. Because of the long relaxation times, the electron system is unstable to "feel" the nonuniformity of the energy barrier, and no nonuniform electron state arises. There is accordingly a change in the order parameter.

When we raise the temperature, there is a progressive emptying of the trapping centers. Since this process is again slow in comparison with the temperature change, however, these centers are effectively overfilled. Moreover, in a commensurate phase there is a density component associated with the uniform order parameter, and the corresponding relaxation would also require some time.

An important point is that a nonuniform density of electrons in trapping centers does not form as the temperature is varied, because of the motion of the incommensurate wave with respect to the lattice.

Figure 1 shows the spatial distribution of the electron density in trapping levels at a given temperature after (1) heating and (2) cooling, according to numerical calculations based on Eq. (2) (for the case of proustite,[5,7] Ag_3AsS_3). The dashed line here is the equilibrium distribution of electrons among trapping levels.

In an incommensurate phase, one also observes partial hysteresis loops. By this we mean when the temperature is varied between two values T_1 and T_2 ($T_1 < T_2$), a hysteresis in the physical properties will also be observed in the incommensurate phase. The following processes occur: During cooling to T_0, the trapping levels fill up to a level m_0, i.e., up to the nonuniform density m_1, after some delay. When heating begins, the electron density first tends toward its equilibrium value, continuing to increase; later, there is a progressive decrease in the density. At the beginning of this process, then nonuniform density decreases first, to the level of the uniform order

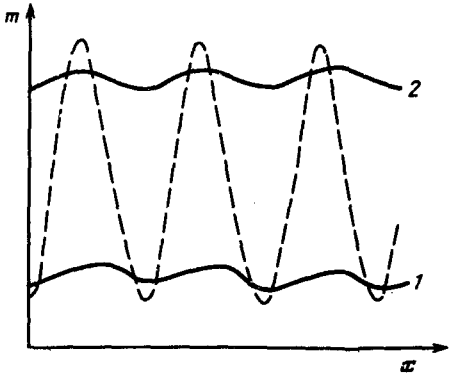

FIG. 1. Results of numerical calculations (for proustite,[5,7] Ag_3AsS_3) based on Eq. (2) for the spatial distribution of the electron density m in trapping levels, for a given temperature after (1) heating and (2) cooling. The dashed line is the equilibrium distribution of electrons among trapping levels.

parameter. The change in the overall concentration then proceeds along the cooling curve. Upon the switch to cooling, the density associated with the order parameter disappears first, and then the process proceeds along the cooling curve. In this manner, a parallelepiped of a partial thermal hysteresis forms.

Taking this approach, we can explain the increase in the difference between the values of observable properties with decreasing temperature. First, the effect which we would expect would be proportional to the square of the order parameter, whose amplitude increase with increasing temperature. Second, as the temperature is lowered, there is a decrease in the probability for heat removal. Correspondingly, the time scales of the relaxation of the electron density to the equilibrium value increase, and again the result is an increase in the effect. The dependence on the rate of change of the temperature and on the initial temperature is obvious: At the lower rates, a greater number of electrons manage to relax to the equilibrium state, and the initial density of electrons in trapping levels depends on the initial temperature.

Taking this approach, we can explain the "reversible" behavior of the hysteresis in Ag_3AsS_3 (proustite). The effect stems from a "memorization" of the uniform part of the electron density in trapping levels.[11] This phenomena is characteristic of all phase transitions in semiconductors.

The magnitude of the effect is also determined by the fact that, according to our estimates, an effective filling of trapping levels occurs in semiconducting crystals of which we are aware, Ag_3AsS_3 and $Sn_2P_2(S_{1-x}Se_x)_6$, in a temperature region in which an incommensurate phase exists. This circumstance also amplifies the effect. One is accordingly led to suggest that the filling of trapping levels could play an important role in the formation of an incommensurate phase as such. As the trapping levels are filled, electrons localize, altering the balance of forces in the crystal, and possibly leading to the formation of an incommensurate phase.

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