PERGAMON

Solid State Communications 115 (2000) 13–17

solid state communications

www.elsevier.com/locate/ssc

Dielectric measurement study of lamellar $CuInP_2Se_6$: successive transitions towards a ferroelectric state via an incommensurate phase?

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Received 10 November 1999; accepted 20 March 2000 by B. Jusserand

Abstract

The dielectric properties of lamellar $CuInP_2Se_6$ are studied as a function of temperature. Two phase transitions are detected: a second-order one at $T_i = 248$ K and a first-order transition at $T_c = 236$ K. These observations confirm the assumed paraelectric and ferroelectric character of the high- and low-temperature phases and give the first indication of an intermediate dipole state existing in this material. The hypothesis of an incommensurate phase occurring between T_i and T_c and the possible appearance of a Lifshitz point in $CuInP_2(Se_xS_{1-x})_6$ are discussed.

Keywords: A. Ferroelectrics; D. Dielectric response; D. Phase transitions

1. Introduction

Chalcogenophosphate crystals built from ethane-like P_2X_6 (X = S, Se) units and off-centering metal cations have been found to exhibit various types of cooperative electric dipole effects [1–10]. $Sn_2P_2S_6$, characterized by a structure with three-dimensional connectivity, is a proper uniaxial ferroelectric that undergoes a second-order transition to the paraelectric phase at $T_0 \approx 337$ K as the Sn(II) ions move to centrosymmetric sites [1]. Replacing sulfur with selenium leads to the solid solution $Sn_2P_2(SexS_{1-x})_6$ for which the state diagram features a splitting at $x > 0.28$ of the second-order transition line $T_0(x)$ into a second-order transition branch $T_i(x)$ and a first-order transition branch $T_c(x)$, which border an intermediate incommensurate (IC) phase [2]. For $Sn_2P_2Se_6$ $T_i \approx 221$ K and $T_c \approx 193$ K. The triple point at $x \approx 0.28$ is a Lifshitz point (LP): the wave vector $\mathbf{q}_m$ of the IC phase modulation decreases continuously to zero as this point is approached by diminishing x. The phase transitions (PT) in $Sn_2P_2S(Se)_6$ occur in the region of crossover from displacive type to order–disorder type transitions [3].

Dipole ordering is observed also in lamellar $CuInP_2S_6$. Below $T_c = 315$ K, the Cu(I) and In(III) ions form polar sublattices shifted in antiparallel directions relative to the layer midplane, thus yielding a *ferri*electric arrangement and a spontaneous polarization normal to the layer [4]. The PT in this system is triggered by the activation of copper motions within a double-well potential (equivalent off-center sites) and has been determined to be of the first-order, order–disorder type (monoclinic space group *Cc* to *C*2/*c*) [5]. The selenium analogue $CuInP_2Se_6$ is a relatively new addition to this class of materials. Calorimetric evidence for the occurrence of a broad PT between 220 and 240 K in this compound was given in a previous paper [6]. More recently, a single-crystal X-ray diffraction study showed that the high- and low-temperature structures of $CuInP_2Se_6$ (trigonal space group *P*-31*c* and *P*31*c*, respectively) are very similar to those of $CuInP_2S_6$ in the paraelectric and ferrielectric phases, with the Cu(I) off-centering shift being smaller in the former than in the latter [7,8]. These findings

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0038-1098/00/$ - see front matter
PII: S0038-1098(00)00131-9

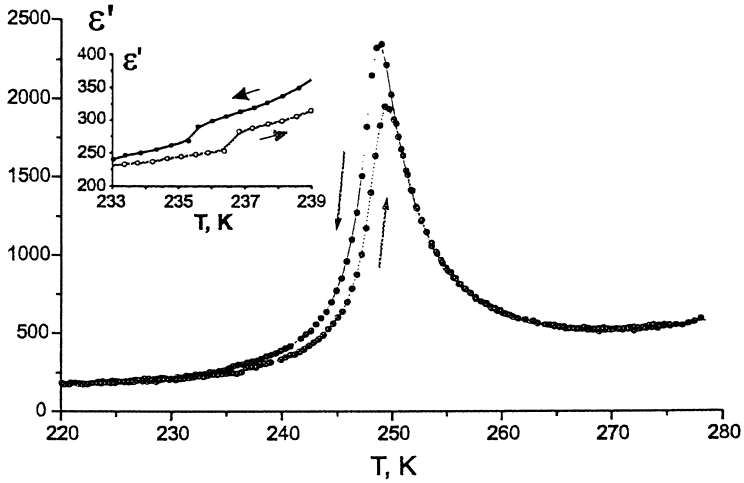

Fig. 1. The temperature dependence of the real part of the electric permittivity ϵ' of $CuInP_2Se_6$ upon cooling and heating. Inset: magnified section of plot around $T = T_c$.

indicate that the transitional effects in the selenium compound, and possibly the solid solution $CuInP_2(Se_xS_{1-x})_6$ merit closer examination.

In this work, we present the first investigation of the dielectric properties of $CuInP_2Se_6$. Our results are consistent with the existence of a high-temperature paraelectric and a low-temperature ferroelectric phase in this material. Importantly, we show that these phases are mediated by two successive transitions: a second-order one at $T_i = 248.5$ K and a first-order transition at $T_c = 235.5$ K. The hypothesis of an IC phase occurring between T_i and T_c and the possible appearance of the LP in the state diagram of $CuInP_2(Se_xS_{1-x})_6$ are discussed.

2. Experimental methods

Crystals of $CuInP_2Se_6$ were grown by the combined techniques of gas transport and recrystallization. The plate-like crystal used was reddish black in color and approximately $5 \times 5 \times 0.1$ mm^3 in size. The dielectric properties were measured by the method of complex resistance at a frequency of 104 Hz and a 10 V cm^{-1} field [10]. Electrodes were made by applying graphite paste to the sample faces perpendicular to the [001] direction, which coincides with the C_3 symmetry axis. The sample temperature was changed at a rate of 0.1 K min^{-1} and controlled with ± 0.1 K accuracy.

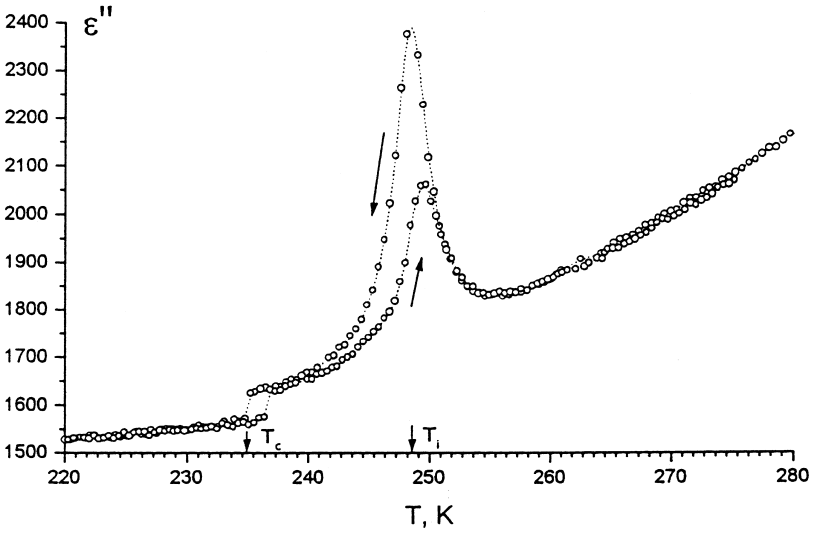

Fig. 2. The temperature dependence of the imaginary part of the electric permittivity ϵ'' of $CuInP_2Se_6$ upon cooling and heating.

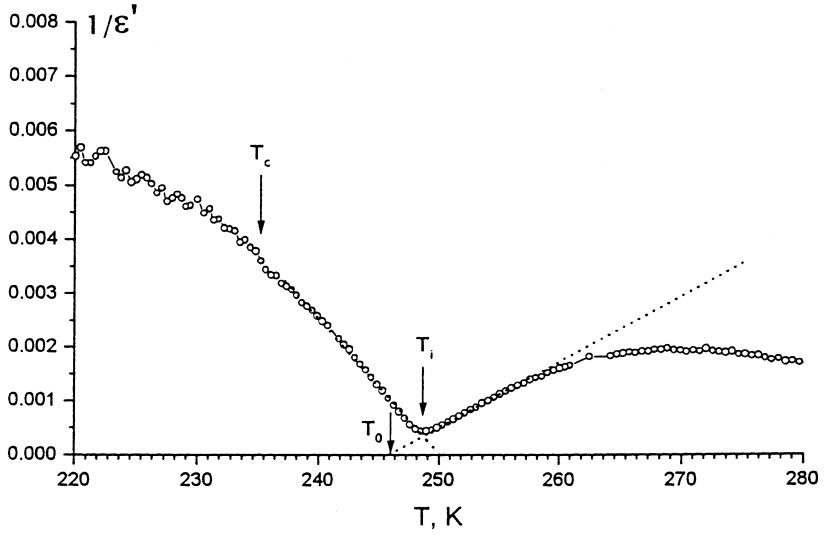

Fig. 3. The temperature dependence of ϵ'^{-1} upon cooling. The dotted lines show the Curie–Weiss curve fits in the paraelectric and intermediate regimes.

3. Results and discussion

The temperature dependence of the real and imaginary parts of the electric permittivity ϵ' and ϵ'' of $CuInP_2Se_6$ are displayed in Figs. 1 and 2, respectively. Both figures show clearly a maximum located at $T_i = 248.5$ K in the cooling cycle. Less visible, but also certainly present, is an anomalous change at $T_c = 235.5$ K in the cooling curves for ϵ' and ϵ''. Thus, two phase transitions rather than a single broad one occur in $CuInP_2Se_6$. The second transition, first revealed here, involves relatively weak effects ($\Delta\epsilon' \approx 50$, $\Delta\epsilon'' \approx 70$ at T_c) that were not detected earlier by calorimetry and diffraction measurements [6]. There is also some discrepancy regarding the first-transition temperature T_i in that it is observed to be several degrees higher in the present work than in Ref. [6]. Such a difference has been noted also in the case of $CuInP_2S_6$ and it appears that lower transition temperatures are generally found when studying fine, polycrystalline samples in place of macroscopic crystals [5,9]. Figs. 1 and 2 essentially confirm the paraelectric and ferroelectric nature of the high- and low-temperature phases, respectively, and provide first evidence for the existence of an intermediate phase at $T_c < T < T_i$ in this material.

The two transitions in $CuInP_2Se_6$ exhibit thermal hysteresis. An increase by 1.5 K in T_c is observed in the lower temperature transition upon warming, implying that this PT is first-order. On the other hand, the hysteretic effects in the $T_c < T < T_i$ regime involve not only an upward shift by ≈ 1.5 K of T_i, but more importantly, a rather large decrease in the values of ϵ' and ϵ'' in almost the entire temperature range during the warming cycle. The latter observation indicates that this PT into the intermediate phase may be second-order.

Analyzing the ϵ' curve for Curie–Weiss (CW) behavior would be informative. In the paraelectric regime, the CW law is found to be valid for $249 < T < 260$ K (Fig. 3). Hence

$$\epsilon' = \frac{C^{\mathrm{I}}}{T - T_0}.$$

where $C^{\mathrm{I}} = 7.5 \times 10^3$K and $1/\epsilon'$ extrapolates to zero at $T_0 = 246$ K. The deviation from CW behavior observed at $T > 260$ K may be attributed to the occurrence of ionic conductivity at these higher temperatures as has been demonstrated for $CuInP_2S_6$ [5,10]; the simultaneous rise of the ϵ'' curve above $T = 260$ K also attests to this. In the intermediate regime, the CW law is satisfied also with $C^{\mathrm{II}} = 4 \times 10^3$ K and $T_0^{\mathrm{II}} = 251$ K (Fig. 3). The values of the Curie constants determined here are of magnitudes characteristic of order–disorder type transitions. They are moreover comparable to those found for $CuInP_2S_6$ (4.7×10^3 K) [5], implying similar electric dipole strengths in the sulfur and selenium compounds. This is as expected given that the same cations, Cu(I) and In(III), contribute to the spontaneous polarization P_s in the two materials, their slightly different off-centering shifts relative to the chalcogen framework leading to a weaker P_s in the selenodiphosphate than in the thiophosphate [7,8].

The question then arises as to the possible nature of the state intermediate between the paraelectric and ferrielectric phases, particularly since no data in the corresponding 230–250 K range were recorded during the recent single-crystal X-ray study [7,8]. It has been shown that the space group of the low-temperature structure $P31c$ (C_{3v}^4) is a subgroup of that of the high-temperature one, $P\text{-}31c$ (D_{3d}^2), with the number of formula units being the same in the two phases. In the ferroelectric regime, P_s appears along the three-fold

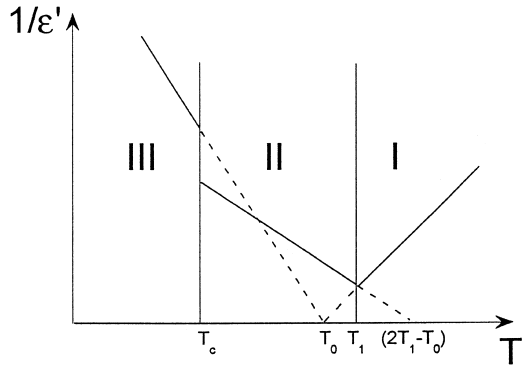

Fig. 4. Reciprocal permittivity in the vicinity of longitudinal LP as calculated in Ref. [13]. Solid curves satisfy the following equations in the: paraelectric phase (I), $\epsilon' = C(T - T_0)^{-1}$; incommensurate phase (II), $\epsilon' = C(2T_1 - T_0)^{-1}$; and ferroelectric phase (III), $\epsilon' = 2C(T_0 - T)^{-1}$.

axis C_3, which determines the disappearance of the inversion center. Thus, taking only the two end-phases into consideration, the order parameter (polar vector $P_s \| Z$) would transform according to the irreducible representation A_{2u} of the point group D_{3d}, and the fluctuations in P_s, according to the representation A_1 of C_{3v}. It may be supposed that the intermediate phase is likewise described by the point group C_{3v}. However, this would imply that the PT at T_c is isostructural and accompanied by a change in the modulus of the vector P_s. Such isostructural PTs are known to be strong first-order transitions [11], which is not the case for the weak feature observed here at T_c.

An alternative hypothesis would be that of an intermediate phase characterized by a modulated structure. Specifically, it may be supposed that T_i marks a transition into an incommensurate (IC) phase and that the PT at T_c is a lock-in transition, i.e. the modulus of the wave vector $\mathbf{q}_m$ describing the modulated space distribution of P_s in the intermediate phase drops to zero upon cooling to T_c. The "noncritical" character of the transition at T_c may then be understood as follows. For proper ferroelectrics (where the transition conserves the unit cell volume, e.g. $NaNO_2$ [12] and $Sn_2P_2Se_6$ [2]), ϵ' in the IC phase is determined by amplitudon and phason contributions. In the one-harmonic sine modulation approximation, the dielectric constant is expected to be smaller at T_c than at T_i: the amplitudon frequency increase upon cooling leads to a dielectric contribution decrease (the phason contribution may increase but only slightly). The dielectric constant may be enhanced by higher harmonic contributions that arise when the modulation profile of P_s in the IC phase becomes domain-like upon cooling to T_c [13]. In $CuInP_2S_6$, a quasi-rectangular dielectric hysteresis loop is measured [4] implying very weakly mobile domain walls and no higher order contributions to ϵ'. $CuInP_2Se_6$ most probably behaves likewise so that ϵ' in the assumed IC phase would be determined only by the amplitudon. In addition, for semiconducting ferroelectrics like these chalcogenophosphates, the mobility of the domain walls in the ferroelectric phase can be drastically reduced by the charge carriers; similar decrease in mobility can occur for "solitons" in the IC phase. This has been illustrated by various compositions within the $Sn_2P_2(Se_xS_{1-x})_6$ system and indeed, a very small anomaly in ϵ' is observed at the lock-in transition (Tc) in one of the more conducting crystals [14]. It is also worth noting that strong thermal hysteresis for the values of the ϵ' and ϵ'' curves in the entire intermediate regime has been observed in the known IC phases of other ferroelectric materials [2,12].

The hypothesis of an intermediate IC phase may be extended to include the possible existence of an LP, i.e. a non-ordering parameter x may be conceived to vary such that the modulation wave vector $\mathbf{q}_m$ decreases continuously to zero as the PT lines $T_i(x)$ and $T_c(x)$ in the T–x diagram converge to a triple point $T(x_0)$ [15–19]. The occurrence of LP behavior in the hexagonal and trigonal crystals were considered theoretically in Refs. [14–16] and found to be very similar. For $P_s \| [001] \| C_3$, two types of LP are possible, each one associated with longitudinal ($\mathbf{q}_m \| [001]$) and transverse ($\mathbf{q}_m \perp [001]$) modulation [17]. Taking the longitudinal case for a magnetic system with short-range interactions, the susceptibility was shown to vary continuously at T_i and to exhibit a small discontinuity at T_c [15]. Moreover, the PT temperatures were found to satisfy the relation:

$$(T_0 - T_c)/(T_i - T_0) \approx 4.4.$$

A weak first-order PT is likewise found in the transverse case, the first-order character becoming stronger as the basal plane anisotropy increases. The critical behavior of uniaxial ferroelectrics with hexagonal symmetry in the vicinity of the LP has been investigated also by renormalization group methods [18,19]; however, this work analyzes only the case of transverse modulation. Note that transverse modulation and LP behavior are observed in the state diagrams of hexagonal crystals of the rare earth metals Tb, Dy and Ho [20,21].

The ratio $(T_0 - T_c)/(T_i - T_0)$ equals 4.2 in the present case and the ϵ'^{-1} curve of Fig. 3 is quite similar in shape to the inverse susceptibility of a longitudinally modulated system considered close to its LP in Ref. [14] (Fig. 4). Fig. 3, however, represents a measurement made far from the LP, if it exists, since the temperature width of the IC phase, $T_i - T_c$, decreases as the LP is approached, i.e. $T_i - T_c \propto (x - x_{LP})^2$, where x_{LP} localizes the LP in the T–x diagram. A comparison may be made with $Sn_2P_2(Se_xS_{1-x})_6$ where $x - x_{LP} = 0.72$ and $T_i - T_c = 28$ K for $x = 1$. Moving towards a supposed LP may be envisioned by varying x progressively in $CuInP_2(Se_xS_{1-x})_6$. The presence of an LP would then be indicated by an increase in the permittivity values along the $T_i(x)$ and $T_c(x)$ lines: $\epsilon'(T_i)$ and $\epsilon'(T_c) \propto |x_{LP} - x|^{-1}$. Investigation of these possibilities should of course be preceded by a diffraction study ascertaining the existence and detailed nature of the IC phase in $CuInP_2Se_6$ between T_i and T_c.

4. Conclusions

Prior to this study, the ferroelectric character of the low-temperature phase of $CuInP_2Se_6$ had been assumed by analogy with $CuInP_2S_6$, but the occurrence of an intermediate, possibly IC phase, was unsuspected. Evidence for the latter given here is, however, far from surprising. Not only is such an IC phase a well-established phenomenon in the closely related system $Sn_2P_2(Se_xS_{1-x})_6$, but layered $CuCrP_2S_6$ is also known to exhibit an intermediate phase, albeit still ill-defined, as it is cooled from the paraelectric ($T > 190$ K) to the antiferroelectric ($T < 150$ K) regime [22,23]. The prospect of an LP appearing in the phase diagram of $CuIn(Se_xS_{1-x})_6$ makes this solid solution a promising model for LP behavior in a quasi-two-dimensional system; moreover, a morphotropic phase boundary may be found therein (monoclinic to trigonal symmetry change). These findings attest to the wealth of cooperative electric dipole effects that can be generated within the lamellar matrix of $CuMP_2X_6$ and portend such further interesting studies in the near future.

Acknowledgements

This work was supported in part by contract no. IC15-CT97-0712 with the European Commission.

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