PHYSICAL REVIEW B **75**, 012303 (2007)

Heterogeneous states observed in the CD_4-CH_4 system

Alexander I. Krivchikov,[1] Piotr Stachowiak,[2,*] Elwira Pisarska,[2] and Andrzej Jeżowski[2]
[1]*Institute for Low Temperature Physics and Engineering, National Academy of Sciences of Ukraine, 47 Lenin Avenue, Kharkov 61103, Ukraine*
[2]*Institute for Low Temperatures and Structure Research, Polish Academy of Sciences, PN 1410, 50-950 Wrocław, Poland*

(Received 23 June 2006; revised manuscript received 10 November 2006; published 29 January 2007)

A hysteresis of the thermal conductivity of $(CD_4)_{1-c}(CH_4)_c$ solid solutions has been detected in the vicinity of the phase transition from partially orientationally ordered phase II to completely orientationally ordered phase III. The temperature interval of the hysteresis increases with the CH_4 concentration increase. An explanation is proposed, which attributes the hysteresis to the existence of a steady mixed two-phase state near the first-order phase transition. The state is observed in a wide range of temperatures.

DOI: 10.1103/PhysRevB.75.012303 PACS number(s): 63.20.−e, 66.70.+f

Thermodynamically stable multiphase states can exist in the vicinity of a first-order phase transition. These heterogeneous states form a complex bulk structure. Type-II superconductors or the intermediate "antiferromagnet-ferromagnet"-type state in a magnetic field[1] are typical examples of such heterogeneous structures. Among other features, the heterogeneous state manifests itself in a hysteresis of some physical properties. Here we report experimental evidence of the hysteresis observed in the thermal conductivity of CD_4-CH_4 solid solutions and a CD_4 pure crystal near the first-order orientational phase transition. While investigating thermal conductivity, we can observe different temperature dependences as the temperature is increased or decreased. Therefore, the hysteresis can be taken as evidence of a steady-state heterogeneous state existing in the molecular system of interacting quantum rotators in a wide enough temperature interval. Thermal conductivity hysteresis—related to the orientational first-order phase transition—was earlier observed in NH_4Cl (Ref. 2) and $NaBH_4$ (Ref. 3) systems but its nature is still obscure.

The CD_4-CH_4 system is a molecular crystalline structure with rotational degrees of freedom. This is a physically interesting quantum object exhibiting strong isotopic effects.[4] The weak anisotropic molecular interaction and the large rotational constant generate considerable quantum effects,[5] first of all because of the high energy of the zero orientational motion of the CH_4 molecules.

Deuterated methane and regular methane are miscible at all concentrations. Three phases, denoted I, II, and III (the last at the lowest temperatures), can be distinguished in the phase diagram of the CD_4-CH_4 solid system at equilibrium vapor pressure. Methane, deuteromethane, and their mixtures exist in phase I in the temperature interval from solidification (90.66 K and 89.78 K, for CH_4 and CD_4, respectively) down to the I→II phase transition (20.4 K and 27.0 K, respectively). In this phase, tetrahedral molecules of both methanes are orientationally disordered.

Under equilibrium vapor pressure, solid methane undergoes a phase transition from orientational phase I (plastic cubic-symmetry phase) to partially orientationally ordered phase II at $T_{\text{I-II}}=20.4$ K. In addition to phases I and II (with $T_{\text{I-II}}=27.0$ K), deuteromethane exists in completely orientationally ordered phase III. Its structure (orthorhombic, space group *Cmca*) is close to that of phase II.[6] The orientational phase transition at $T_{\text{II-III}}=22.1$ K is a first-order phase transition with a volume jump of 0.63%,[6,7] which is considerably larger than that at the I-II phase transition. Phase III also appears in CD_4-CH_4 solid solutions. It exists, at equilibrium vapor pressure, in a wide range of temperatures and CH_4 concentrations (up to $c \approx 0.85$).[9] The appreciable differences between the rotational constants and the total nuclear spins of CD_4 and CH_4 molecules, as well as weak molecular field, can provoke strong thermal fluctuations of the molecular field upon approaching the phase transition temperature.[8] Since the rotational motion of the CH_4 molecules and the translational vibrations of the crystal lattice interact with each other, the thermal conductivity can be a very sensitive tool of investigation of the orientational phase transitions in methane.[10–12] This paper reports an experimental investigation of the thermal conductivity of $(CD_4)_{1-c}(CH_4)_c$ solid solutions with concentrations $c=0-0.78$ near the temperature of the first-order orientational phase (II-III) transition.

The experiments were carried out using the home-designed setup described earlier.[13] The procedure of growing and cooling the CD_4-CH_4 crystals was similar to that in Ref. 12. The thermal conductivity coefficient (κ) was determined in range from 10 K to 25 K by the steady-state heat flow method. The temperature and its gradient along the sample were measured with two germanium thermometers fixed 12 mm apart from each other. The relative error of the thermal conductivity measurement was no more than 6%. The statistical error did not exceed 2%.

Results of the measurements are shown in Fig. 1. The thermal conductivity temperature characteristics obtained for the CD_4-CH_4 samples with $c=0$, 0.22, 0.6, and 0.78 of CH_4 at rising and lowering temperatures display a hysteresis only near $T_{\text{II-III}}$ (Fig. 1).

The thermal conductivity versus temperature curve $\kappa(T)$ is independent of heating or cooling at temperatures much higher or much lower than $T_{\text{II-III}}$. Here we avoid deliberately the question of the CH_4 influence upon the $\kappa(T)$ dependence in three phases of solid CD_4-CH_4 solutions. This will be discussed in a separate publication. We only restrict ourselves to noting that the thermal conductivity of phase II, $\kappa_{\text{II}}(T)$, is independent of both temperature and CH_4 concentration. In phase III, $\kappa_{\text{III}}(T)$ increases exponentially at lowering temperature (what is typical for dielectric crystals) and

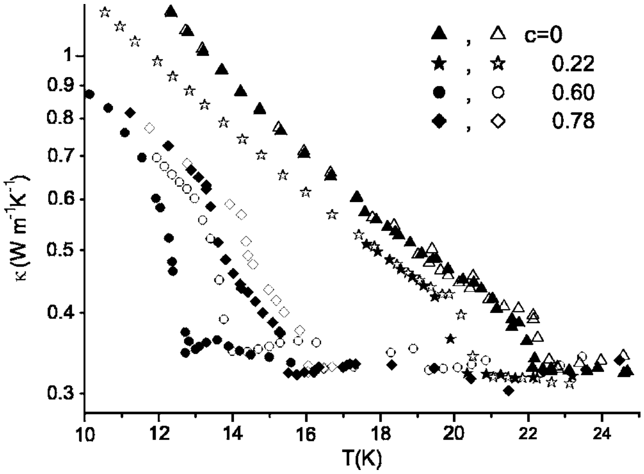

FIG. 1. Thermal conductivity of $(CD_4)_{1-c}(CH_4)_c$ for $c=0$, 0.22, 0.6, and 0.78 at rising (open symbols) and lowering (solid symbols) temperatures in the vicinity of orientational phase transition II-III.

decreases at growing concentration in the whole interval $c=0-0.78$. Smoothed values of the thermal conductivity in the vicinity of the II-III phase transition are shown in Fig. 2. Marked are the points which characterize the process of phase transformation. At decreasing temperature, phase III appears at point T_2 and phase II disappears at point T_3. When the temperature increases, phase II appears at point T_4 and phase III disappears at point T_1. In the T_3-T_1 interval there exists a quasisteady mixed state of the two phases. In this region of temperatures, $\kappa(T)$ measured at the same temperature is independent of time (at least during a 24-h period of observation). Upon the change from cooling to heating (and vice versa) in the interval T_3-T_1, the curve $\kappa(T)$ takes the opposite course and becomes weakly dependent on temperature. The inverse behavior is temperature reversible if the temperature changes only inside the hysteresis—i.e., the curve is reproducible—irrespective of whether the temperature rises or lowers.

As the concentration c increases, the hysteresis of $\kappa(T)$ shifts towards low temperatures and is now observed in a wider interval of temperatures and κ values. Figure 3 illustrates a part of the $(CD_4)_{1-c}(CH_4)_c$ phase diagram containing the parameters of the hysteresis (T_1, T_2, T_3, and T_4). Our results depicted in the phase diagram agree well with literature data[9,14,15] and provide much supplementary information about the region of existence of the heterogeneous state. It is

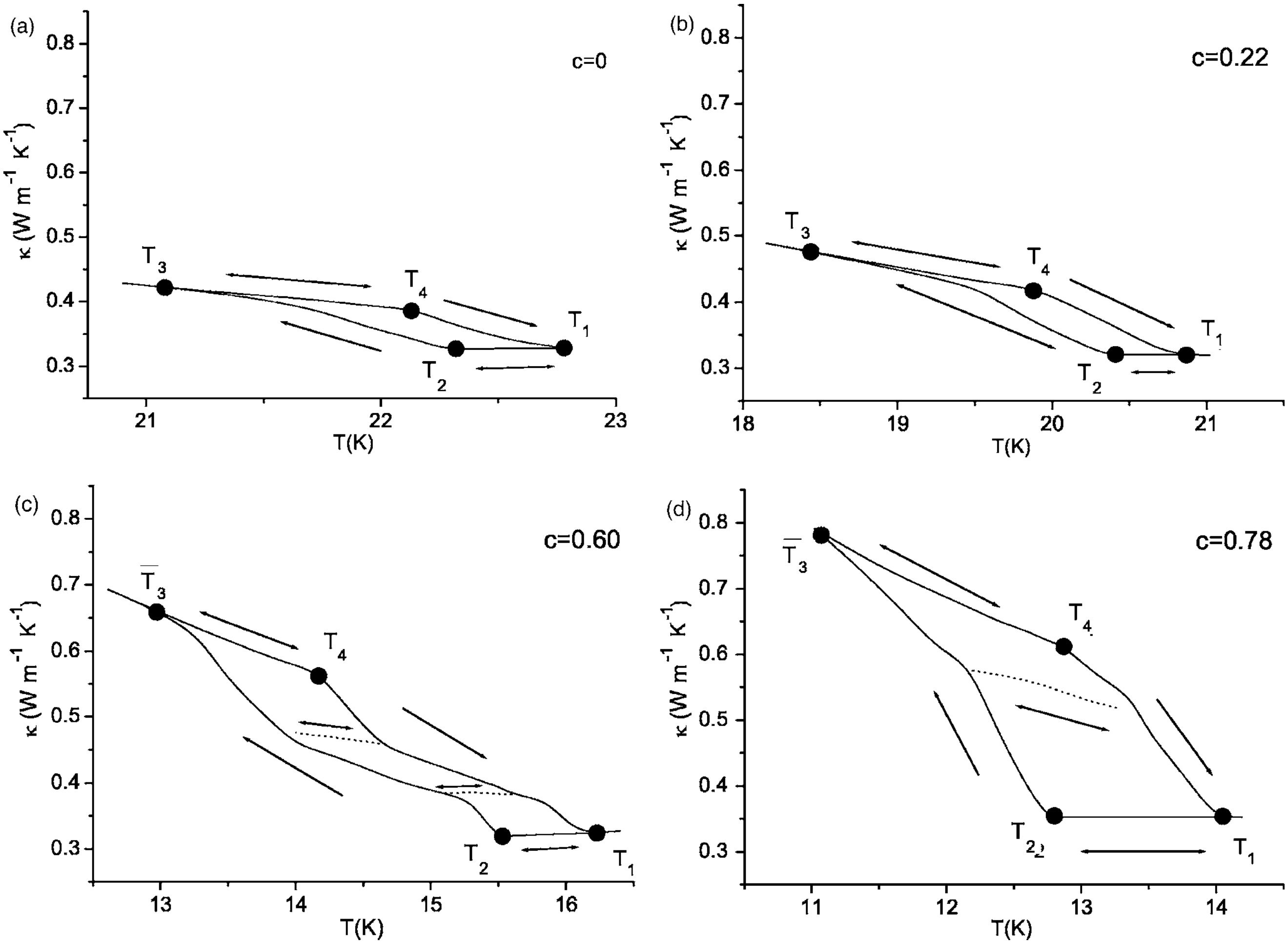

FIG. 2. The hysteresis of thermal conductivity of $(CD_4)_{1-c}(CH_4)_c$ for $c=0$, 0.22, 0.6, and 0.78, in the vicinity of orientational phase transition II-III. Points T_2, T_3 (decreasing temperature) and points T_4, T_1 (increasing temperature) correspond to the beginning and the finish of the phase transition. Arrows show the direction of temperature change.

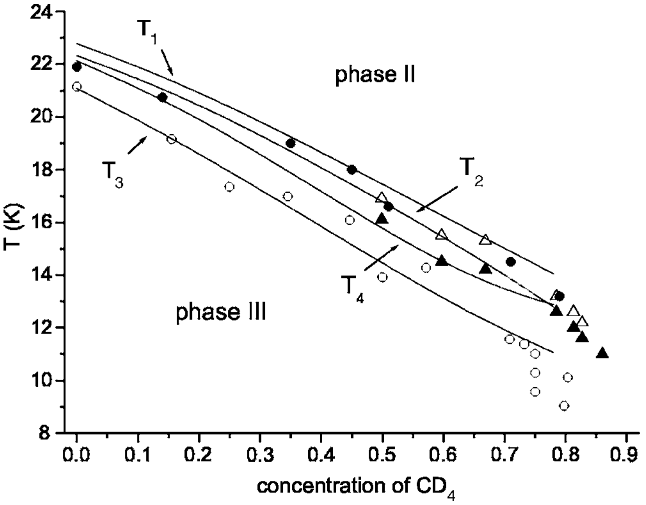

FIG. 3. Part of the phase diagram of CH_4-CD_4 solid solutions. We show here the temperature of the phase transition II-III in dependence on the concentration of CD_4 in the mixed crystal $(CD_4)_{1-c}(CH_4)_c$ obtained from a fixed thermal conductivity (solid lines), from x-ray scattering (○) (Ref. 15), from NMR (△,▲) (Ref. 9), and from heat capacity (●) (Ref. 14) measurements.

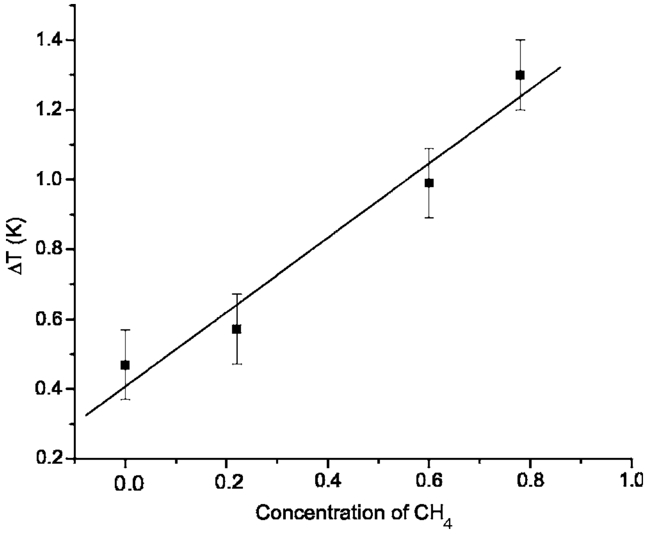

FIG. 5. The half width of the hysteresis of the volume fraction in dependence on the concentration of CH_4 in the mixed crystal $(CD_4)_{1-c}(CH_4)_c$. The solid line represents a least-squares fit by a linear dependence.

fundamentally important that this heterogeneous state is quasistationary and remains stable when the temperature changes in the opposite direction. The heterogeneous state can be considered as a mixed two-phase state in which phase II and phase III coexist. In the region of the mixed two-phase state, the thermal conductivity is actually the effective thermal conductivity $\kappa_{\text{eff}}(T)$ determined by the thermal conductivities of the two phases and volume fraction of phases. The curve $\kappa_{\text{eff}}(T)$ can, to some extent, be influenced by the complex spatial structure of the mixed state which changes with the phase concentration. The temperature dependence of the volume fraction $q(T)$ accounts for the phase correlation in the mixed two-phase state in the course of phase transformation and is a sound estimate of the order parameter. The $q(T)$ values, calculated using the models of heat transfer in heterogeneous states (geometric averaging, Adler averaging[16] and effective medium method[17]), are very similar. According to the geometric model commonly used to describe heterogeneous states, the effective thermal conductivity of the mixed state is the geometric mean of the thermal conductivities of two phases: $\kappa_{\text{eff}}(T)=\kappa_{\text{II}}^{1-q}\kappa_{\text{III}}^{q}$, where q is the volume fraction of phase III. The dependence $q(T)$ calculated within the geometric mean model for different c values is shown in Fig. 4. The curve $q(T)$ illustrates how the concentration of the phases varies during phase transformation at growing and lowering temperatures. When the temperature changes in the reverse direction (see the dotted curves), the volume fraction remains constant within the region of the hysteresis. The reverse change in the temperature (heating ↔ cooling) is indicative of the existence of a long-living mixed state in this region of temperatures. The width of this T interval increases near linearly with the CH_4 concentration (see Fig. 5).

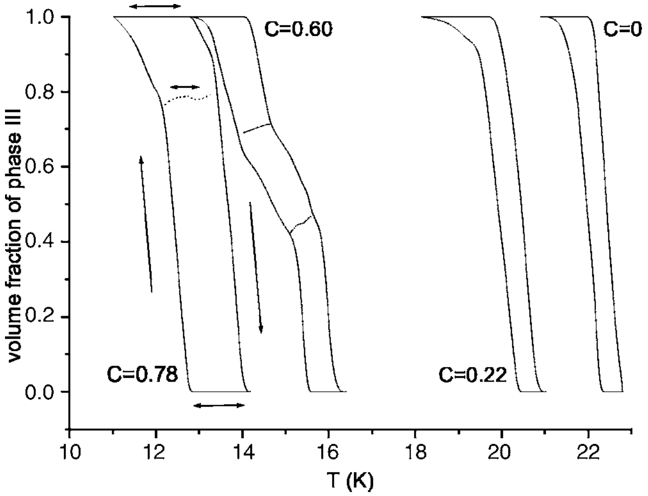

FIG. 4. The temperature dependence of the volume fraction of phase III in the mixed two-phase state, obtained from the thermal conductivity data for four concentrations of deuteromethane. The arrows show the direction of the temperature changes.

The observed thermal conductivity hysteresis shows that the orientational phase transition between the partially ordered phase and the completely ordered phase is realized through a mixed two-phase state and proceeds as a continuous transformation. The width of the temperature interval in which the mixed state exists increases with the CH_4 concentration in the CD_4-CH_4 solution increase. The continuous phase transition is realized under the condition of small interphase surface energy against the background of strong temperature and pressure fluctuations in the presence of defects. The transition is attended by the formation of a complex inhomogeneous bulk structure.[18,19]

The authors are grateful to V. G. Manzhelii, A. I. Prokhvatilov, and M. Prager for fruitful discussions. This work was supported by the Polish State Committee for Scientific Research.

*Corresponding author: p_stach@int.pan.wroc.pl

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