The Sites of Premelting in Organic Compounds

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Bartis recently proposed a theory which should allow to determine whether impurities or defects are responsible for the premelting phenomena in crystalline solids. We have tested this model on several orientationally disordered molecular crystals studied by proton NMR spectroscopy. This showed that extended defects, and more likely grain boundaries are at the origin of the premelting phenomena in these crystals.

1. Introduction

Since many years it is well established that point defects or extended defects, such as vacancies, dislocations or grain boundaries play an important role in the melting process of crystalline solids. Several theories have been proposed to explain the premelting effects in these solids [1–8]. In this paper, the defect theory of Bartis [4–8] is tested on several orientationally disordered molecular crystals.

2. Bartis's Theory

In this theory, a crystal is considered as an isotropic elastic continuum, stresses around defects causing a variation of the local effective pressure and consequently changing the melting temperature in these regions of the crystal. This model was first proposed by Bartis to explain the anomalous behaviour of thermodynamic properties such as the specific heat C_p, the thermal expansivity α or the compressibility K_T near the melting point. C_p should vary with temperature following a power-law, the exponent of which depends on the nature of the defects involved in premelting [4, 6]: C_p should be proportional to $(T_m - T)^{-2}$ if the liquid grows near point defects, and to $(T_m - T)^{-3}$ if dislocations are implied in the premelting process. T_m is the melting point of the crystal. These equations are consistent with experimental results obtained by Gronvold on bismuth and selenium [9, 10]. The variation of the thermal expansivity α with pressure should follow the same power-law with exponents equal to -2 or -3 if the defects involved are point or extended defects, respectively, and this is in good agreement with piezothermal measurements on 1,4-butane-diol and benzene by Fuchs et al. [11].

However, the separation of Raoult impurity effects from those due to defects is very difficult because impurities also cause variations of thermodynamic properties following similar power-laws.

More recently, assuming that the liquid phase forms cylindrical domains along the dislocations and that the melting temperature varies linearly with the stresses, Bartis suggested that the size of the cylindrical domains goes as $(T_m - T)^{-1}$. By consequence, the volume of the molten domains should go as $(T_m - T)^{-2}$ [7, 8]. In the same way, assuming that the stresses are inversely proportional to the cube of the distance from an impurity and that the liquid phase forms spherical domains around the impurities, the radius of these spherical liquid domains should go as $(T_m - T)^{-1/3}$ [8]. According to these assumptions, the temperature of the sample should vary linearly with $F^{-1/2}$ or F^{-1} if the premelting effects are due to extended defects or impurities, respectively [8]. F is the molten fraction of the sample.

3. Results and Discussion

A Nuclear Magnetic Resonance (NMR) proton wide-line study of several orientationally disordered, so-called "plastic", molecular crystals has been undertaken.

The study of solid thiophene by Rousseau et al. showed that, several degrees below the melting point,

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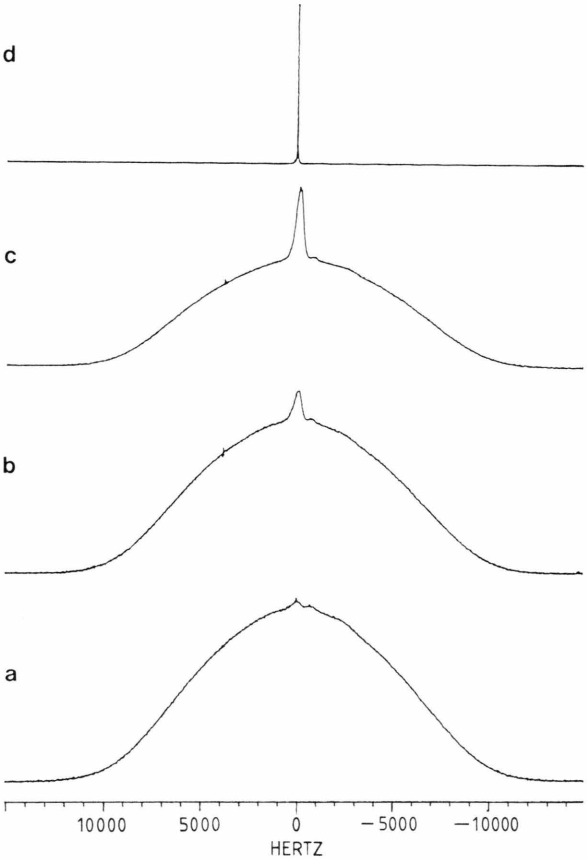

Fig. 1. Evolution of the proton NMR line near melting in a polycrystalline sample of benzene (99.98 purity): a) $T_m - 5$ K; b) $T_m - 1$ K; c) $T_m - 0.1$ K; d) supercooled liquid, $T_m - 3$ K, T_m is the melting point.

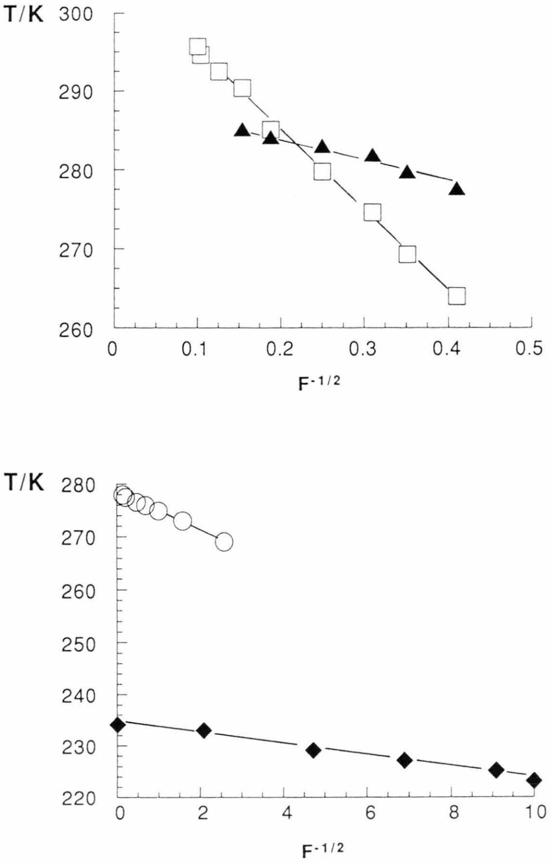

Fig. 2. $F^{-1/2}$ dependence of the temperature: ○ benzene, ◆ thiophene, ▲ 1,4-dioxane, □ cyclohexanol. F is the molten fraction of the sample.

a narrow line of ~ 500 Hz appears on the broad line of ~ 10 000 Hz characteristic of an orientationally disordered crystal [12]. The intensity of the narrow line increases with temperature and its width remains constant up to the melting point, where the liquid appears suddenly. This narrow line was attributed to molecules which experience fast self diffusion. The variation of the fraction of mobile molecules with $(T_m - T)$ follows a power-law with an exponent of -1.9. This value suggested that, in this case, the premelting effects are probably not due to Raoult impurities only, but are caused by the presence of extended defects in the crystal.

Polycrystalline benzene behaves like thiophene (Figure 1) [13]. The study of samples of different purity allowed to show that the mobile molecules are located at grain boundaries, forming a thin film at the interfaces between grains. These premelting effects are enhanced by the presence of impurities, but according to our interpretation premelting is located at grain boundaries even in the absence of solid – insoluble impurities. This view of premelting as an interface initiated process is supported by the well known surface melting observations on pure single crystals of metals [14] or on thin layers of methane adsorbed on graphite or magnesium oxide [15].

This is also in agreement with the defect theory of Bartis. Here, the defects involved in the premelting phenomena of thiophene and benzene are presumably grain boundaries.

A similar behaviour was observed in other crystals such as 1,4-dioxane and cyclohexanol [16].

Plots of the temperature versus $F^{-1/2}$ and F^{-1} were obtained for these four plastic crystals (Figs. 2 and 3). In all cases, the data are best fitted by a straight line for the plot of T versus $F^{-1/2}$ (Fig. 2).

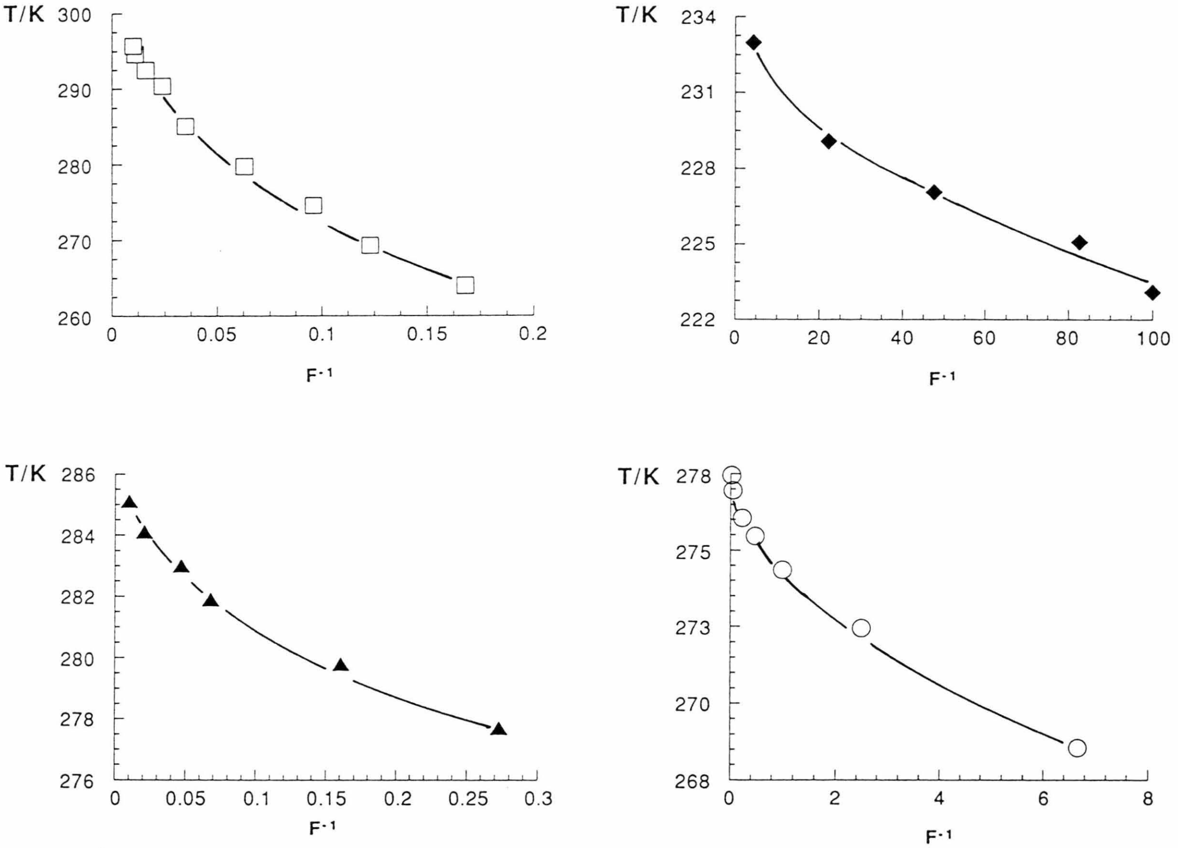

Fig. 3. F^{-1} dependence of the temperature: ○ benzene, ◆ thiophene, ▲ 1,4-dioxane, □ cyclohexanol.

These results are consistent with our interpretation of the premelting effects in orientationally disordered molecular crystals and confirm the fact that, in these materials, extended defects and more likely grain boundaries rather than impurities are responsible for the premelting effets, in good agreement with Bartis theory of defects.

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