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ORIENTATIONAL PHASE TRANSITIONS IN ALLOYS

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INTRODUCTION

Complex intermetallic phases such as Frank Kasper, Laves and Zintl compounds have local structural units of high symmetry, often tetrahedral or icosahedral. Such systems can undergo both translational and orientational disorder, leading to a variety of possible phases, shown schematically in Figure 1. They tend to have a semiconducting electronic structure, characterized by a small gap (or pseudo-gap) at the Fermi surface and leading to relatively high resistivities (10^3-10^4 mΩ cm).

Quasicrystals, a novel kind of matter with long-range orientational, as opposed to translational, order, have been the subject of a considerable body of recent work. The possibility of the converse situation, translational without orientational order, is also not without interest: plastic crystals have been known for eighty years or more in organic systems and inorganic ones with complex ligands, but not, to our knowledge, been found in an intermetallic system. This paper will briefly review our recent discoveries of plastic crystal behavior in high-temperature solid phases of the semiconducting alloys CsPb (1,2) and NaSn (3).

THERMODYNAMICS

CsPb and NaSn belong to a class of Zintl compounds in which charge transfer and directional bonding leads to the formation of M_4^{4-} (M = Pb or Sn) Zintl ions in both solid and liquid (4,5). Drop-calorimetric studies in our laboratory have shown that both CsPb (6) and NaSn (7) exhibit two transitions near the melting point with comparable changes in entropy ΔS (Fig. 2.). The measured transition temperatures are T_1 = 596°C, T_2 = 647°C for

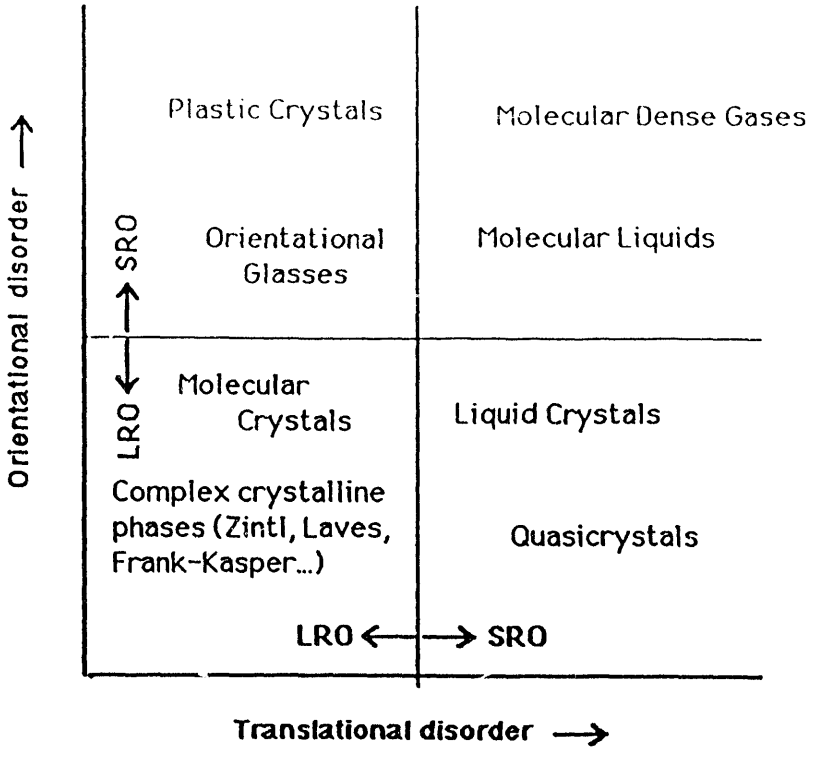

Figure 1. Types of order and disorder in condensed matter

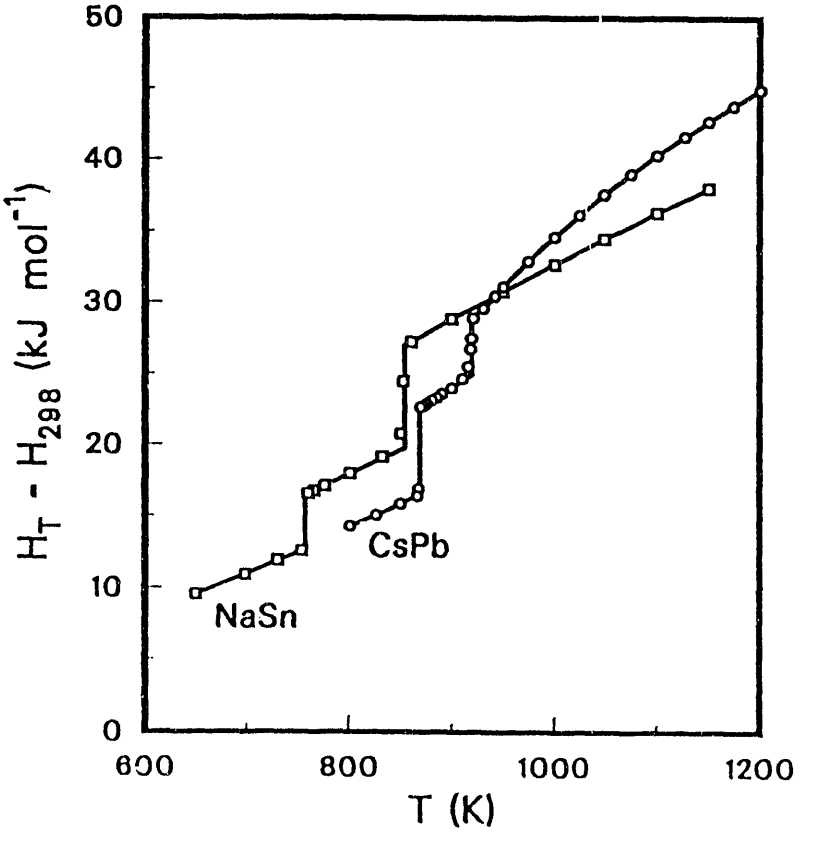

Figure 2. Enthalpy of NaSn and CsPb

CsPb and T_1 = 484°C, T_2 = 581°C for NaSn. The other lead and tin compounds in the same class exhibit only one in the range of temperature investigated, extending about 100° below the melting point. The phase diagram of CsPb (8) is inconclusive regarding the existence of more than one phase at the equiatomic composition (Fig.3). The large disagreement in the melting points determined from calorimetry 647°C and from liquidus (620°C) precludes any correlation between the phase diagram and the thermodynamics. On the other hand, in an early study of NaSn (9, Fig. 4), Hume-Rothery identified a phase transition which he characterized simply as a "polymorphic phase transformation in the solid". The temperature T_1 of this transition and T_2, that of the solid-liquid transition, were 483°C and 578°C respectively, very close to the values found in the calorimetric measurements (7).

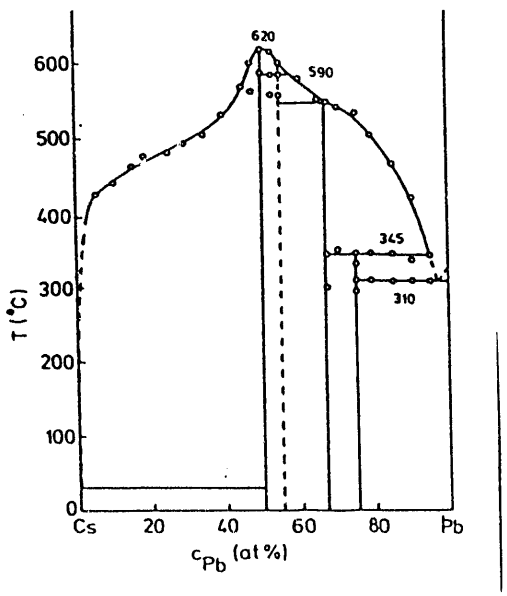

Figure 3. Phase diagram of Cs-Pb.

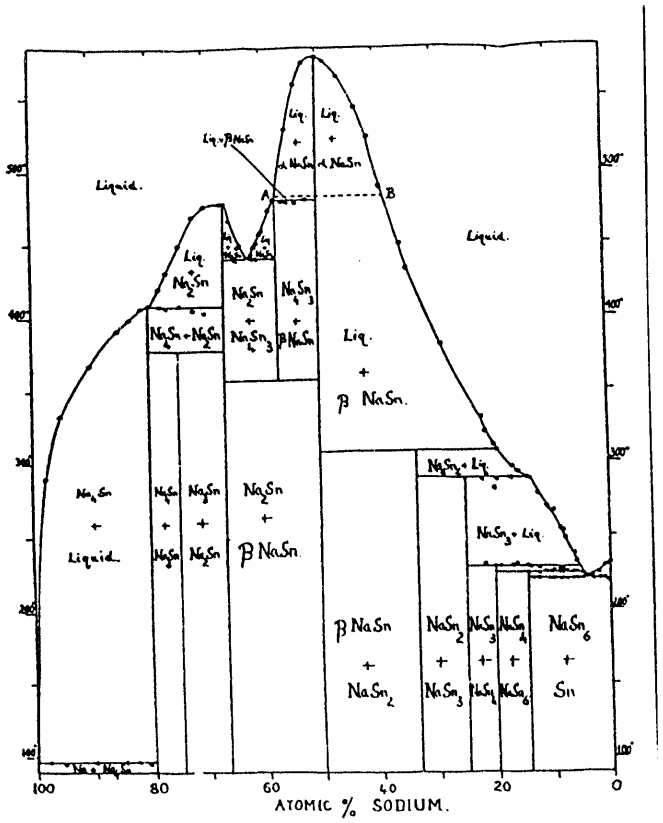

Figure 4. Phase diagram of Na-Sn (Hume-Rothery)

The electrical transport and thermodynamics of NaSn are quite different from those of CsPb. Liquid CsPb remains in the semiconducting regime while liquid NaSn becomes semimetallic. The heat capacity of liquid CsPb in the vicinity of the melting point is extremely large, about 10 times that is expected from additive behavior, while the heat capacity of liquid NaSn is only slightly larger, by about a factor of 2.

To resolve the nature of intermediate phase in CsPb, we made neutron diffraction measurements (4) in all three phases, which following Hume-Rothery we will label β ($T<T_1$), α ($T_1<T<T_2$) and ℓ ($T_2<T$). The β phase revealed a crystalline powder pattern for which Rietveld analysis gave the crystal structure shown in Fig. 5. It is analogous to that found for NaPb by Marsh and Schoemaker (10) and shows well defined Pb_4^{4-} tetrahedral Zintl ions enclosed by larger, oppositely directed Cs_4^{4+} tetrahedra, leading to Cs_4Pb_4 structural units. At small Q, ~ 1 $Å^{-1}$, there is an unresolved double Bragg peak. In the α phase this peak persists but the rest of the diffraction pattern is diffuse, so a crystal structure determination is impossible. In the ℓ phase the entire pattern is diffuse, but there is a relatively sharp peak at the wave vector Q of the first Bragg peak in the solid. This peak, a "first sharp diffraction peak" (FSDP), is a signature of large structural units in the liquid, which we have identified with the survival of Cs_4Pb_4 structural units (4,6).

NaSn has a homologous crystal structure (11) and in the liquid phase shows a similar FSDP observed by Alblas et al. (12). No diffraction measurements have been made, to our knowledge, in the α phase.

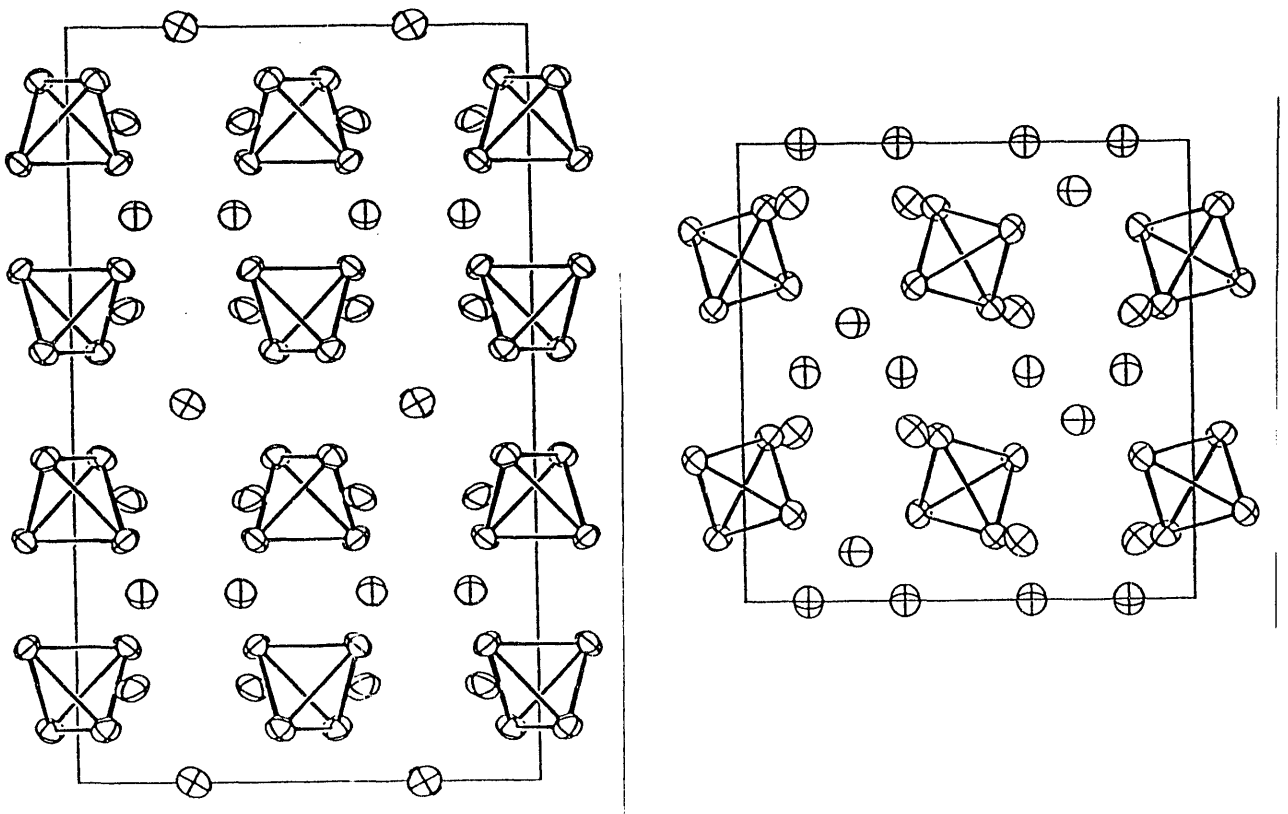

Figure 5. Crystal structure of CsPb

a) Projections onto a-c plane b) Projection onto a-b plane.

The diffuse nature of the diffraction pattern in CsPb at higher Q suggest a dynamic disorder. We therefore carried out quasielastic neutron scattering measurements at the Institute Laue Langevin. As expected, the β phase showed no energy broadening of the elastic peaks, while the ℓ phase showed broadened peaks characteristic of diffusion in the liquid. On the other hand in the α phase the scattering was composed of a combination of elastic and broadened components. The Q dependence of the elastic and broadened components is shown in Fig. 6, together with the results of a simple model calculation based on random jump reorientations of Cs_4Pb_4 structural units between the four orientations observed in the β phase (1,2). The good fit between data and model calculations indicates that the α phase is a plastic crystal characterized by jump reorientations of structural units. The peak in the quasielastic intensity at Q ~ 0.9 $Å^{-1}$ suggests that the Cs atoms are involved in the dynamical process since a large interatomic distance is required to reproduce a peak at

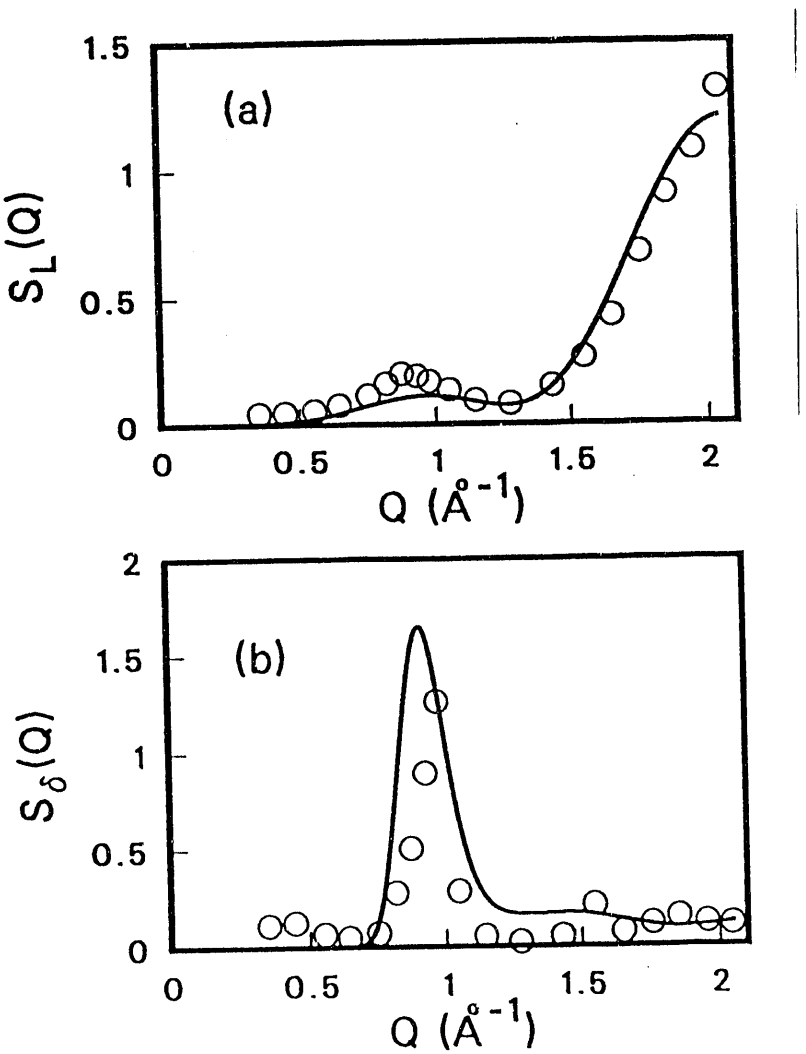

Figure 6. Structure factors for quasielastic scattering from CsPb at 600-630°C.
(a) Lorentzian (b) δ-function

this Q. However, the large entropy change at the transition, $\Delta S_1 = 7.15$ J mol^{-1} K^{-1}, suggests that the Cs atoms are not rigidly bound to the Pb_4^{4-} tetrahedra during the reorientation.

Recent measurements of quasielastic scattering from NaSn at the ISIS pulsed neutron source at Rutherford Appleton Laboratory (U.K.) show a broadened component (3), the intensity of which is given in Fig. 7. In this case the elastic diffuse scattering is close to zero and varies randomly with Q. This situation is similar to that observed in the high-temperature phase of C_{60} where quasielastic broadening is explained on the basis of rotational diffusion (13). This is quite feasible for a relatively isotropic molecule like C_{60} but somewhat unexpected for a structural unit of tetrahedral symmetry which is found in NaSn, at least in the β phase. Examination of the different possible diffusion mechanisms (i.e. rotational diffusion, hindered rotation or jump reorientation) is underway.

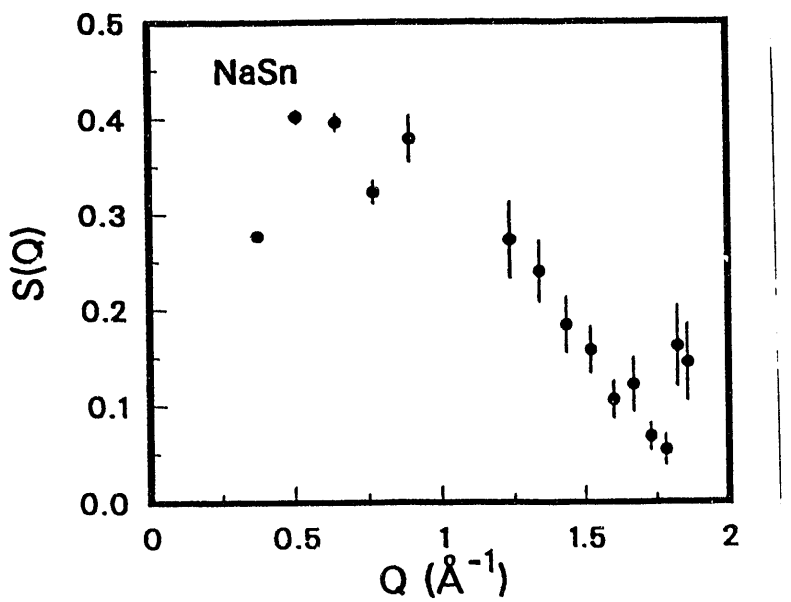

Figure 7. Structure factor for quasielastic scattering from NaSn at 500°C.

CONCLUSIONS

Plastic crystal behavior is observed in CsPb and NaSn at high temperature. This behavior is associated with M_4^{4-} or A_4M_4 structural units (A = Cs or Na, M = Pb or Sn) orientationally disordering at a temperature T_1, about 50 °C below the melting point T_2 where translational disorder sets in. The nature of the orientational disorder appears to be different in the two phases, exhibiting jump reorientations in CsPb and a more isotropic behavior in NaSn. In other Zintl compounds such as KPb, there is a single melting point where orientational and translational disorder sets in simultaneously. The classification of the

different Zintl compounds into these two different kinds of behavior will require detailed calorimetric measurements over an extended range below the melting point, or alternatively neutron diffraction or quasielastic scattering measurements just below it.

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