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Physics in the fast lane: rotors, fast ions and mobile fermions

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Abstract. Dynamic disorder in the high-temperature solid phases of the Zintl compounds CsPb and NaSn is characterized by fast orientational motions of the polyanions and coupled motions of the cations. Melting is characterized by slow translational motions of the centres of mass of the polyanions. The dynamic behaviour of the ions is associated with dramatic increases in electrical conductivity characteristic of the behaviour expected of a mixed conductor.

1. Introduction

Melting of a crystalline solid into a liquid is generally thought of as a disordering process from a state in which the atoms execute thermal motions about static equilibrium sites to one in which they all migrate randomly over the whole space occupied by the material. In a complex system, several different components of this disordering may be distinguished: these can include translational disorder of one sublattice, chemical disorder between two or more sublattices, orientational disorder of molecules or complex ions, and lattice melting in one or two directions in the crystal. When such a system is heated towards the melting point, different dynamical disordering processes set in until complete long-range disorder

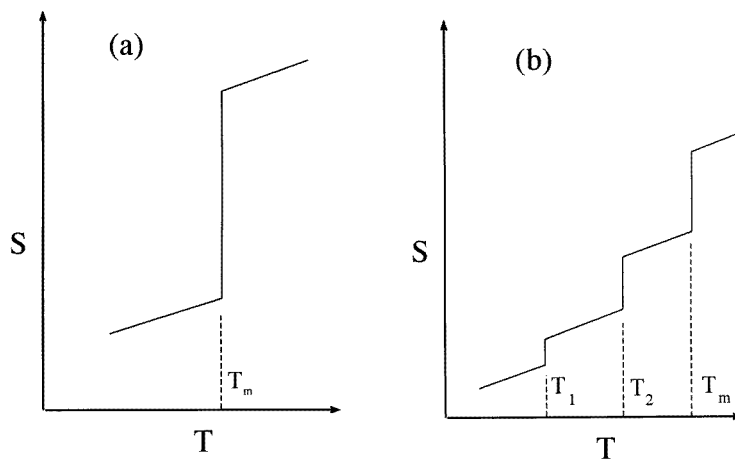


Figure 1. Schematic illustrations of the melting process in which different disordering processes set in (a) at the same temperature or (b) at a sequence of distinct temperatures.

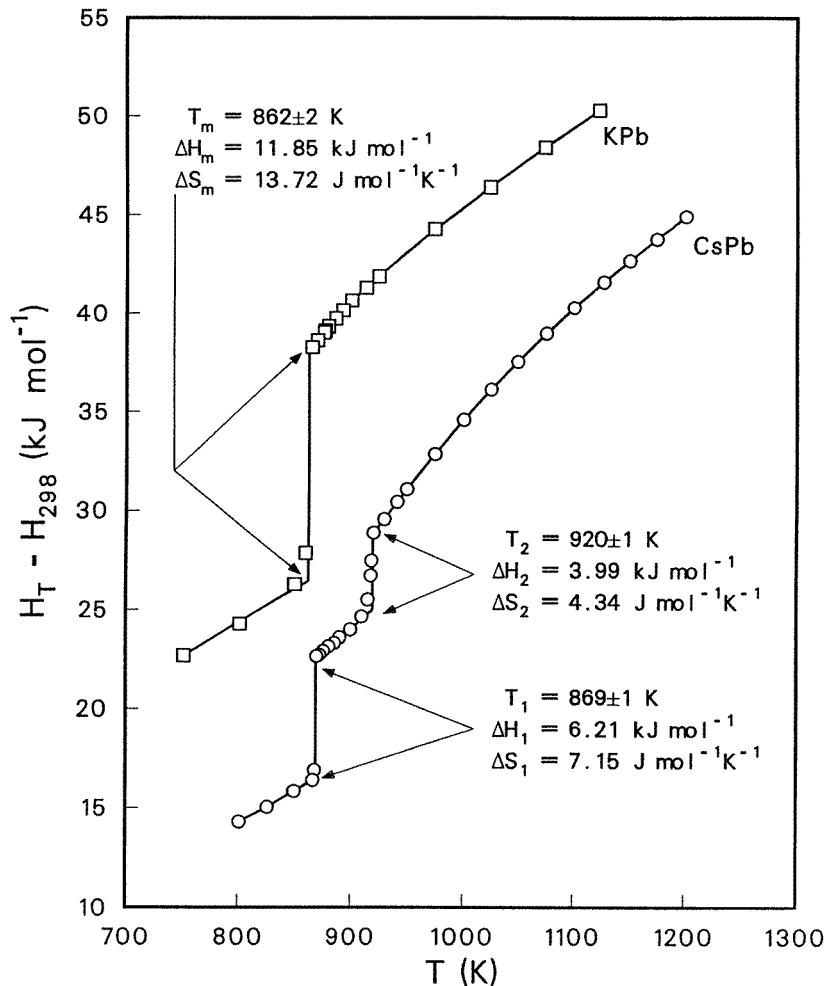


Figure 2. Enthalpy as a function of temperature near the melting points of alkali-lead compounds [2]. The solid lines are a guide to the eye.

is achieved in the liquid state. Further distinctions can be made as to whether a particular disordering process occurs gradually, over an extended temperature range, or suddenly, at a phase transition. If more than one process is associated with a phase transition, these transitions may occur at a single temperature—the melting point (figure 1(a))—or a sequence of distinct temperatures (figure 1(b)) culminating in the melting point. In either case the entropy of melting may be decomposed into a sum of partial entropies associated with the different disordering processes:

$$\Delta S = \Delta S_1 + \Delta S_2 + \cdots + \Delta S_m.$$

Along with the atomic structure changes taking place in this way, changes in the transport properties and response functions of the systems, such as electronic conduction thermopower, Hall effect, magnetic susceptibility and ionic conduction, may be expected. These changes may occur either abruptly at a phase transition or gradually over a temperature

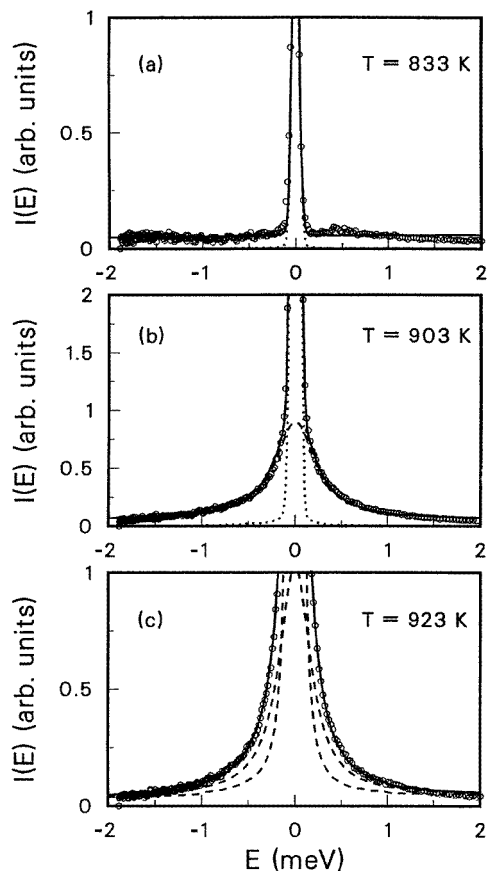


Figure 3. Quasielastic neutron scattering spectra for the three phases of CsPb in the vicinity of the phase transitions shown in figure 2. Circles: data; solid lines: fitted delta and Lorentzian functions, broadened with the experimental energy resolution function [3].

interval between transitions.

Zintl compounds of the form A_mM_n , where A is an electro-positive (alkali or alkaline-earth) metal and M is an electro-negative element, provide a rich ground for investigating this kind of behaviour. In these compounds, charge transfer from A to M leads to chemical properties characteristic of elements one or two columns to the right of M in the periodic table, often involving directional bonding and the formation of complex anions. They generally behave as semiconductors or semi-metals in both the solid and the liquid state, and exhibit a rich variety of transport properties, bonding and structure as a function of composition, temperature and pressure.

2. Dynamically disordered solid phases

A typical example of differences in melting behaviour is provided by the equiatomic alkali-lead compounds studied by Saboungi and co-workers, which form tetrahedral Pb_4^{4-} Zintl ions in both solid and liquid [1]. Figure 2 shows the enthalpy as a function of temperature for KPb, which exhibits a single transition, and CsPb, which exhibits two transitions about 50 K

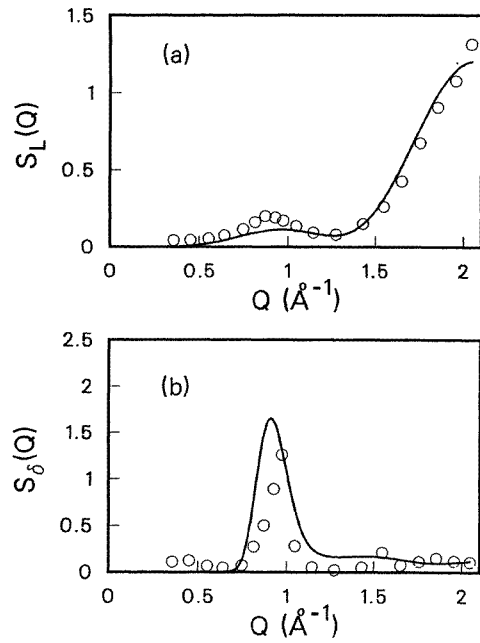


Figure 4. Structure factors for (a) Lorentzian and (b) delta-function peaks in the disordered solid phase of CsPb (880 K). Circles: data; solid lines: results from the model described in the text [3]. The calculated structure factor in (b) has been broadened with the instrumental Q -resolution function.

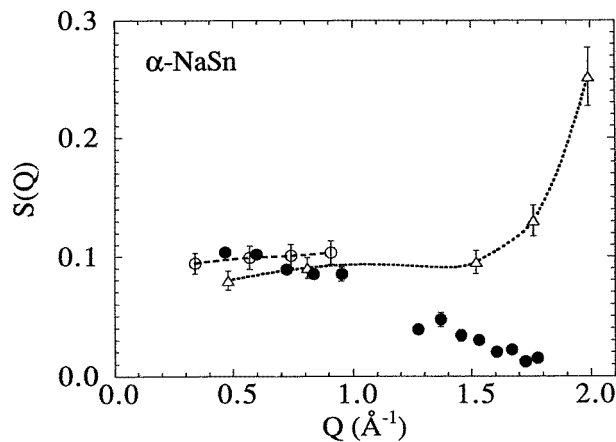


Figure 5. Structure factors for Lorentzian peaks in the disordered solid phase of NaSn (773 K). Solid circles: high-resolution data from IRIS; open circles: medium-resolution data from HET (neutron energy: 20 meV); open triangles: low-resolution data from HET (neutron energy: 40 meV) [5]. The lines are a guide to the eye.

apart [2]. To investigate the disordering processes involved, quasielastic neutron scattering (QENS) measurements were carried out at the Institut Laue-Langevin [3], typical results of which are shown in figure 3. The spectra in the low-temperature (clearly crystalline) phase

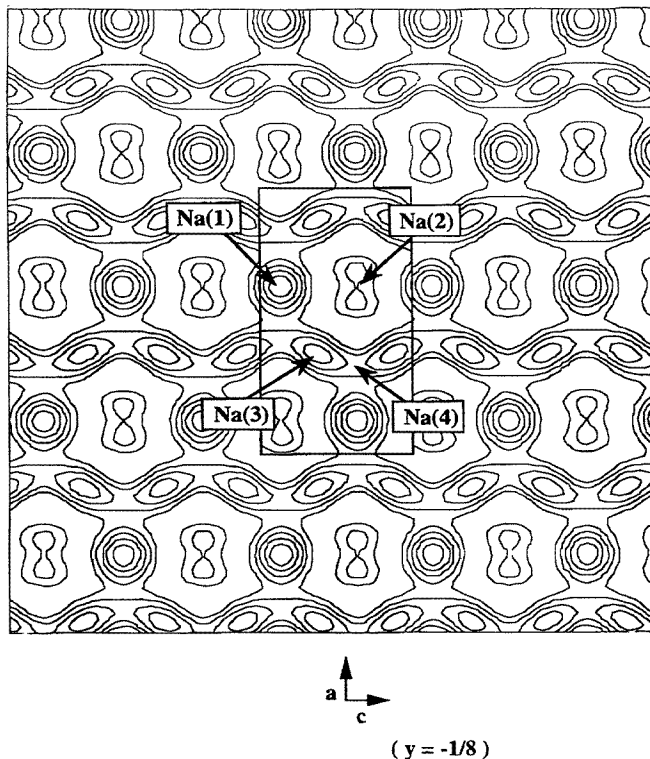


Figure 6. Fourier contour maps of the neutron diffraction in the ac -plane of the disordered solid phase of NaSn at 753 K [7]. Na(1) and Na(2) are the fixed sites and Na(3) and Na(4) the mobile sites associated with the rapid Na^+ migration.

(a) could be fitted nicely by a delta function convoluted with the instrumental reduction function, those in the intermediate phase (b) by a combination of delta and Lorentzian functions, and those in the high-temperature (clearly liquid) phase (c) by a combination of two Lorentzians. These results show immediately that the phase intermediate between the two phase transitions is a solid phase characterized by some kind of dynamic disorder.

The structure factors (intensities as a function of the scattering vector Q) of the two peaks are shown in figure 4. Both sets of data are compared with theoretical curves based on a highly simplified model in which Cs_4Pb_4 units, which can be identified in diffraction results [4] from the crystalline phase, exhibit random jump reorientations between the four orientations observed in the crystal. The excellent agreement between this simple model and the data shows that the disordered solid is a rotor phase involving both Cs^+ and Pb_4^{4-} motions.

Similar results for the disordered solid phase in NaSn [5], obtained at ISIS, are shown in figure 5. NaSn is chemically analogous to CsPb, forming Sn_4^{4-} Zintl ions in solid and liquid [6]. The neutron results, however, are somewhat different: in the QENS spectra (figure 5) obtained from measurements made at the high-resolution back-scattering spectrometer IRIS and at the lower-resolution chopper spectrometer HET at two different incident neutron energies, two Lorentzians of different widths can be distinguished at scattering vectors $Q > 1 \text{ \AA}^{-1}$. Furthermore, elastic scattering is not observable except for the intense Bragg

scattering at around 1 \AA^{-1} , despite the large incoherent scattering cross section of Na. These results indicate that the dynamic disorder in NaSn consists of fast reorientations of the Sn_4^{4-} Zintl ions together with a slower translational migration of the Na^+ cations [5]. Despite their different time constraints, the two processes must be coupled since only a single phase transition is observed.

3. Structure of the disordered solids

Neutron diffraction measurements on the two disordered solid phases just discussed show that the Bragg scattering observed around a wave vector of 1 \AA^{-1} is in fact composed of several distinct peaks. This implies crystal structures of relatively low symmetry, surprising since orientational disorder usually proceeds into cubic phases. Diffraction data from the disordered phase of NaSn, taken at IPNS [7], show that this phase is in fact orthorhombic, so the overall crystal symmetry is actually lowered at the disordering transition.

Rietveld analysis of the diffraction profiles provides a detailed confirmation of the general picture inferred from the QENS data: the Sn_4^{4-} Zintl ions are actually found to occupy two different sites, each with two different orientations, each configuration being occupied one quarter of the time. The Na^+ cations occupy four different sites, of which two are fixed (presumably helping to maintain the framework of the crystal) and two are mobile, providing pathways for rapid migration parallel to the c -axis of the orthorhombic cell. These pathways exhibit pronounced convolutions parallel to the a -axis (figure 6).

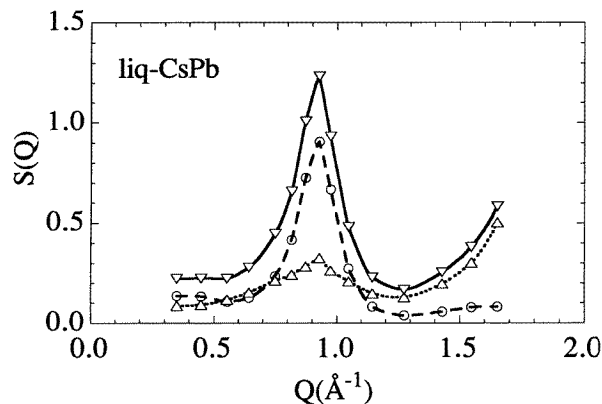


Figure 7. Structure factors of the narrow (circles) and broad (triangles) Lorentzian peaks, and total intensities (inverted triangles), for liquid CsPb at 923 K [5]. The lines give a guide to the eye.

4. Dynamic disorder in the liquids

Comparison of the QENS data for the disordered solid and liquid phases gives insight into the final disordering that takes place on melting [5]. In CsPb, the structure factor of the elastic scattering in the disordered solid phases, shown above in figure 4(b), is mimicked by that of the narrower component of the two Lorentzians fitted to the QENS spectra of the liquid (figure 7). The energy widths of the two components differ by about a factor of 8. It is reasonable to associate the narrow component with translational diffusion of the centres

of mass of the Pb_4^{4-} Zintl ions and the broad component with the rotational diffusion of these units and associated motions of the Cs^+ cations.

In liquid NaSn, the structure factors of the peaks observed in the IRIS and HET measurements follow clearly the behaviour observed in the disordered solid phase, shown above in figure 5, the most significant difference being that the Bragg peaks at around 1 \AA^{-1} are no longer observed [5]. As in the disordered solid phase, it is reasonable to associate the narrow component with the centre-of-mass motions, now including those of the Sn_4^{4-} Zintl ions as well as of the Na^+ cations, and the broad component with the Zintl-ion reorientations.

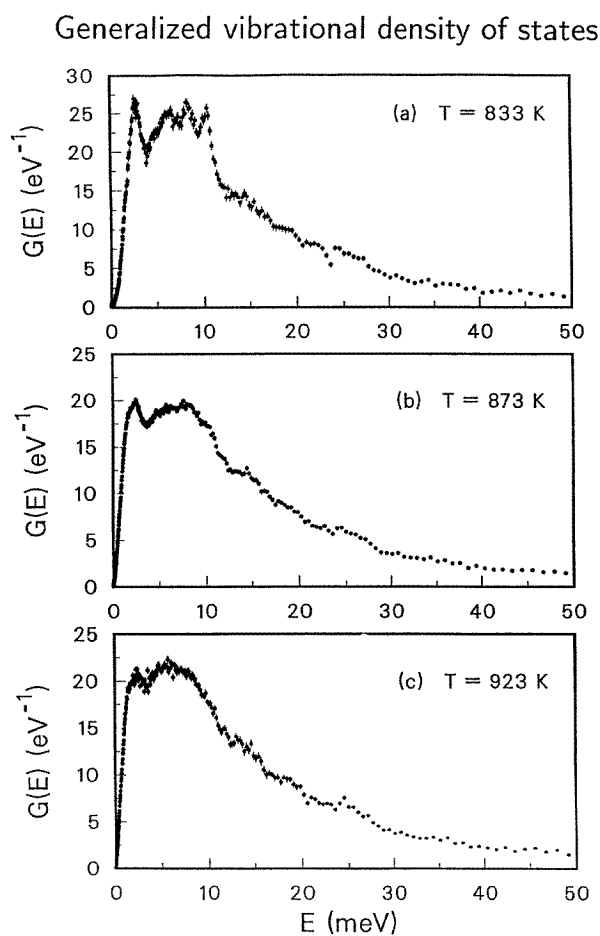


Figure 8. The generalized vibrational densities of states in the three phases of CsPb [3].

5. Vibrational aspects of the disorder

Dynamic disorder can be expected to influence the dynamics on shorter time-scales. The characteristics of the vibrational spectra in the three phases of CsPb [3] are shown in figure 8. A regular tetrahedron possesses three normal modes with frequencies in the ratios $1:\sqrt{2}:2$

(for central forces between the constituent atoms). The Pb_4^{4-} Zintl ions can be expected therefore to exhibit a librational mode and three vibrational modes. These can be clearly identified in figure 8(a). As the temperature is increased into the disordered solid (b) and liquid (c) phases, the distinction between orientational and vibrational modes is maintained, although separate vibrational modes can no longer be identified.

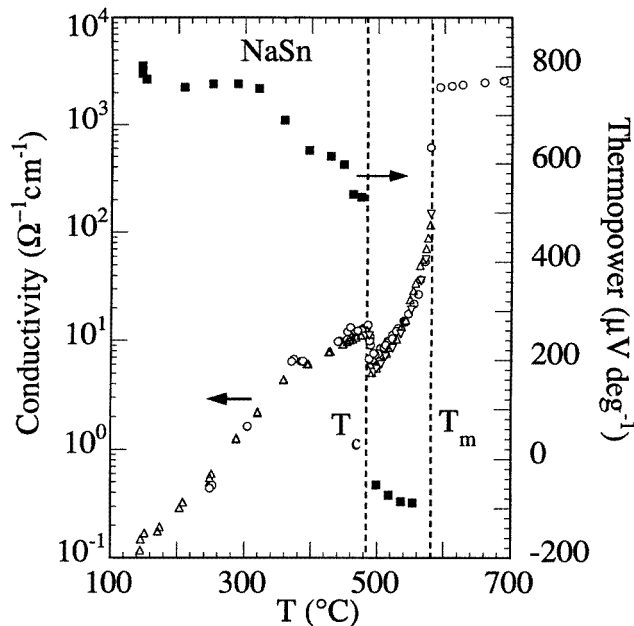


Figure 9. Electrical conductivity and thermopower as a function of temperature in NaSn [8].

6. Electrical conductivity

In a semiconducting compound with a small band gap one would expect a rather subtle interplay between atomic disorder and electronic transport: on the one hand the disorder would tend to increase the scattering of mobile electrons or holes and hence decrease the conductivity, while on the other hand the gap between valence and conduction bands would be expected to decrease, leading to enhanced conductivity. Both effects are in fact observed in the compounds discussed here. A typical behaviour is that of NaSn [8] shown in figure 9. The conductivity shows a typically activated behaviour as temperature is increased in the ordered crystal, drops at the disordering transition and then rises by 2–3 orders of magnitude until the melting point is reached, after which it increases relatively slowly. In CsPb [8] there is instead a large increase by nearly two orders of magnitude at the disordering transition followed by a slow rise up to the melting point. The general problem of ‘mixed’ conduction, involving interacting fast ions and mobile fermions, has been discussed on a phenomenological basis by Ramasesha [9], who finds a distinction between the ‘wide-gap’ situation characterized by a gradual increase with temperature in the population of mobile ions and fermions and the ‘narrow-gap’ situation where both exhibit a jump increase at the disordering transition. In the present context, NaSn appears to represent the wide-gap case

and CsPb the narrow-gap case. A similar distinction is found in other mixed conductor systems, e.g., between Ag₂Te in the one class and Ag₂S and Ag₂Se in the other [10].

7. Conclusions

Dynamic disorder in the high-temperature solid phases of the Zintl compounds CsPb and NaSn is characterized by fast orientational motions of the polyanions and coupled motions of the cations. In CsPb these appear to be on a similar time-scale, while in NaSn the orientational motions are more rapid. The cation motions in NaSn appear to be of a translational type in which the Na⁺ ions migrate through the crystal along pathways parallel to the *c*-axis. In both cases melting is characterized by the appearance of slow translational motions of the centres of mass of the polyanions.

The dynamic behaviour of the ions is associated with dramatic increases in electrical conductivity. Here again the detailed behaviour shows significant differences, with CsPb exhibiting the behaviour expected of a narrow-gap mixed conductor and NaSn that of a wide-gap mixed conductor.

Acknowledgments

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