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Reorientations in plastic crystal phases of Zintl alloys

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Quasielastic neutron scattering measurements on the Zintl alloy NaSn show that the high-temperature solid phase discovered by Hume-Rothery is a plastic crystal characterized by rapid rotations of the Sn_4^{4-} Zintl ions. The reorientations are similar to those previously observed in CsPb but have a markedly different wave vector dependence, indicating a different behaviour of the alkali metal ions.

1. Introduction

Zintl alloys of lead and tin with the heavier alkali metals are semiconductors with surprising and unusual properties in both solid and liquid states [1,2]. These are ascribed to the formation of M_4^{4-} Zintl ions arising from charge transfer and covalent bonding around the polyvalent metal atoms. These polyanions exhibit both rotational and translational order, leading to a variety of complex dynamical behaviours, which can involve (a) translational motions of the polyanions and cations, (b) rotations of the polyanions about their centers, and (c) vibrational motions of the atoms within the polyanions.

CsPb and NaSn are two members of this class of alloys which exhibit especially complex behaviour. Drop-calorimetric studies at Argonne have shown that both CsPb [3] and NaSn [4] undergo two transitions near the melting point with comparable changes in the entropy ΔS at each transition (fig. 1). Other Zintl alloys that have been measured show only one melting transition. In a previous quasielastic neutron scattering (QENS) study of CsPb carried out on the IN6 spectrometer at the ILL, it was shown that the intermediate phase, between 596°C and 647°C, is a plastic crystal characterized by rapid rotations of the Pb_4^{4-} Zintl ions, apparently accompanied by large displacements of the Cs^+ cations [5].

This paper presents preliminary results on a similar study of NaSn. In an early study of this alloy, Hume-Rothery [6] identified a phase transition at 483°C that he characterized simply as a "polymorphic transformation in the

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Fig. 1. Enthalpy of CsPb [3] and NaSn [4].

solid". This present work shows that this transition is from a regular crystal to a plastic crystal or "rotator phase", similar to that established in CsPb. However, significant differences are observed in the detailed microscopic behaviour.

2. Experiments and results

QENS experiments were carried out on the IRIS spectrometer at the ISIS pulsed spallation source. Graphite [002] analysers were used, giving a final energy of 1.858 meV and an energy resolution of about 0.015 meV. A valuable feature of this instrument is a total scattering detector at 170° , which makes it possible to monitor the structural changes rapidly as the temperature is changed. By following the largest-d Bragg peaks, changes in crystal structure at 484°C and melting at 581°C were observed on both heating and cooling, consistent with the calorimetric measurements [4]. In the α phase, above the transition at 484°C , Bragg peaks were not observable above $Q = 2.5 \text{ \AA}^{-1}$, and substantial diffuse scattering appeared above $2 \text{ \AA}^{-1}$, similar to the behaviour observed in the corresponding phase in CsPb [5] and strongly suggestive of plastic crystal behaviour. QENS scans were made in the liquid at 600°C and in the α (500°C) and β (400°C) solid phases after cooling from the melt. The liquid phase showed the usual broadening associated with translational diffusion, with de Gennes narrowing in the vicinity of the peak in the structure

Fig. 2.

Fig. 3.

Fig. 2. Intensity of a single Lorentzian fit to the quasielastic scattering from NaSn (α phase, 500°C).

Fig. 3. Energy width of a single Lorentzian fit to the quasielastic scattering from NaSn (α phase, 500°C).

factor around $Q = 1 \text{ \AA}^{-1}$. The β phase showed only sharp peaks with the resolution width of the instrument. In between, the α phase showed quasielastic broadening over the entire Q range investigated. The intensity and energy width of the QENS, derived from the data by a maximum entropy analysis [7], are plotted as a function of Q in figs. 2 and 3, respectively. It can be seen that both intensity and width increase with Q up to maxima that occur around 0.7 and 1.2 $\text{\AA}^{-1}$, respectively. Both then fall to minima around 1.7 $\text{\AA}^{-1}$ and then rise sharply up to the Q limit of the measurements.

Elastic scattering is observed only in the vicinity of the Bragg peaks around $1.0 \text{ \AA}^{-1}$, where it is so strong that the quasielastic intensity and width are hard to measure accurately. For other Q values the elastic scattering is zero within statistical error.

3. Discussion

The behaviour of the total scattering in the α phase resembles that of CsPb and suggests a plastic crystal or rotator phase associated with rapid reorientations of the Zintl ions, in this case Sn_4^{4-} . However, the detailed behaviour of the QENS is different from that of CsPb, which could be satisfactorily fitted on the basis of a simple model of jump reorientations between the four orientations observed in the crystal at low temperature [5]. A similar model for NaSn does not explain the observed behaviour. In particular, the absence of diffuse elastic scattering is not consistent with purely jump reorientational motions.

This is especially true for the case of NaSn where the substantial incoherent scattering associated with the Na nuclei (about 20% of the total scattering) would lead to diffuse elastic scattering if the Na ions undergo only reorientational motions about fixed centres. The observation of only quasielastic scattering, without a significant elastic component, shows that the Na ions are undergoing rapid migration through the crystal. The rapid rise of the energy width of the QENS at small Q is consistent with such behaviour. In contrast, the rapid rise in the intensity and width of the QENS above $1.7 \text{ \AA}^{-1}$ may reflect the reorientational motion of the compact Sn_4^{4-} structural units.

More detailed analysis of the QENS and elastic scattering behaviour will be given in a forthcoming publication.

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