

## Two-Stage Melting in Cesium Lead Alloys

David L. Price, Marie-Louise Saboungi, and Rick Reijers<sup>(a)</sup>

Argonne National Laboratory, Argonne, Illinois 60439

Gordon Kearley and Ross White

Institut Laue-Langevin, 38042 Grenoble, France

(Received 10 December 1990)

The intermediate phase of the intermetallic alloy CsPb is shown to be a plastic crystal characterized by jump reorientations of  $\text{Cs}_4\text{Pb}_4$  structural units. The wave-vector variation of elastic and quasielastic intensities is well reproduced by a simple model of independent structural units jumping between the four orientations observed in the crystal at room temperature. This represents the first observation of a plastic-crystal phase in a metal alloy.

PACS numbers: 64.70.Kb, 61.50.Ks

Equiatomic alloys of alkali metals with lead and tin form highly ordered structures in both the solid and liquid states.<sup>1,2</sup> Transfer of approximately one electron per atom from the alkali to the heavy metal atom leads to covalent bonding and the formation of tetrahedral  $\text{Pb}_4^{4-}$  or  $\text{Sn}_4^{4-}$  complexes. The existence of these complexes, first proposed by Zintl in the 1930s, explains the unusual structures of these alloys in solid and liquid states and their remarkable electrical transport<sup>3</sup> and thermodynamic<sup>4</sup> behavior.

The systematics of the alkali-metal-lead alloys  $A\text{Pb}$  have been studied with neutron diffraction,<sup>1</sup> electrical resistivity,<sup>3</sup> and calorimetric measurements.<sup>5</sup> The crystal structures in the solid can be described in terms of  $\text{Pb}_4$  tetrahedra surrounded by larger, oppositely directed  $A_4$  tetrahedra. The liquid structures are well represented in terms of the random packing of these  $A_4\text{Pb}_4$  units. As the size of the  $A$  atom increases, the structural units

become more stable, and electron transfer takes place more predominantly within the units rather than through the network as a whole.<sup>6</sup> These properties are most pronounced in the end member of the series, CsPb, which has an unusually high resistivity,<sup>7</sup>  $7000 \mu\Omega\text{cm}$ , and large negative temperature coefficient,  $-115 \mu\Omega\text{cm/K}$ , in the liquid, characteristic of a type-III semiconductor in the scheme of Mott and Davis.<sup>8</sup>

CsPb is unusual also in its melting behavior, which appears to take place in two stages. The calorimetric results of Saboungi *et al.*,<sup>5</sup> reproduced here in Fig. 1, revealed two transitions at 869 and 920 K, with comparable entropy changes,  $\Delta S = 0.86R$  and  $0.52R$ , respectively. A similar behavior in NaSn was noticed by Hume-Rothery and ascribed to a "polymorphic transition of the compound NaSn."<sup>9</sup> In the expectation that the lower transition in CsPb was of this type, neutron diffraction measurements were made at 880 K in the intermediate phase during the work described in Ref. 1. The measured structure factor, shown in Fig. 2, resembles to a large extent that taken in the liquid at 930 K. However, the first diffraction peak is sharper and more pronounced than in the liquid and can be ascribed to a Bragg reflection (or two unresolved reflections) broadened by the resolution of the diffractometer. However, no further Bragg peaks can be identified, making it impossible to

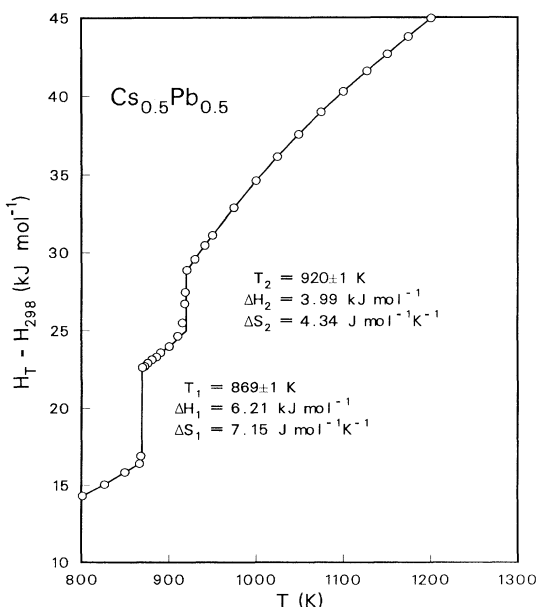


FIG. 1. Enthalpy of CsPb as a function of temperature (Ref. 5).

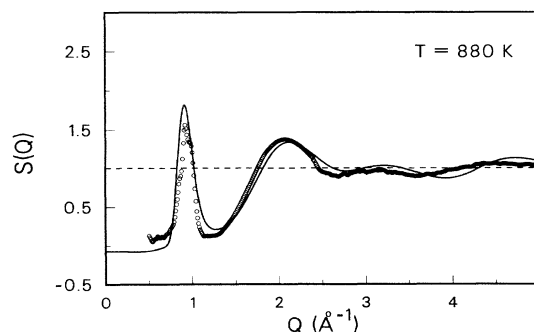


FIG. 2. Measured structure factor of CsPb at 880 K (circles). The solid line shows the structure factor for the model described in the text.

determine the crystal structure of this phase if, indeed, it exists.

The fact that this behavior is observed only in CsPb out of all the alkali-metal-lead alloys indicates that a steric factor may be involved. The larger size of the Cs atom makes the  $\text{Cs}_4\text{Pb}_4$  structural units more spherical and more capable of rotation,<sup>10</sup> suggesting the possibility that the intermediate phase may be a plastic crystal with structural units located on a crystal lattice while undergoing rapid reorientation.

To investigate this possibility, quasielastic scattering measurements on CsPb were carried out on the IN6 spectrometer<sup>11</sup> at the Institut Laue-Langevin (ILL). The CsPb alloy, prepared by techniques described in Ref. 5, was powdered and loaded into a sample holder consisting of three Zircalloy tubes, 9.5 mm i.d., 120 mm long, with 0.6 mm wall thickness, mounted in a vanadium furnace on the spectrometer. The line joining the centers of the tubes was oriented at  $45^\circ$  in transmission to the incident beam, which was masked to an area 2 cm wide  $\times$  5 cm high. An incident neutron wavelength of 5.12 Å was chosen, enabling quasielastic measurements out to a wave vector  $Q = 2.05 \text{ \AA}^{-1}$ , just below the maximum of the second peak in  $S(Q)$ . Measurements were made in the low-temperature phase at 300 and 833 K, in the intermediate phase at 873, 888, and 903 K, and in the liquid phase at 923 K. At 873 K two runs were

made, before and after melting the sample: No discernible difference was observed. Time-of-flight data were collected in nineteen groups of detectors with scattering angles ranging from  $16.6^\circ$  to  $112.9^\circ$ . The equivalent  $Q$  range for elastic scattering was  $0.35\text{--}2.05 \text{ \AA}^{-1}$ . The scattering from an equivalent array of empty tubes was subtracted from the sample scattering, after making a correction for the sample attenuation factor. Scattering from a vanadium plate reference sample was used to provide a relative intensity calibration as a function of angle and define the instrumental energy resolution. An absolute intensity calibration was made by comparing the  $S(Q)$  data obtained by integration over energy with the data of Fig. 2, which themselves were normalized with the condition that the neutron-weighted average  $\langle S(Q) \rangle \rightarrow 1$  as  $Q \rightarrow \infty$ .

Representative quasielastic energy spectra for the three phases are shown in Fig. 3. It is seen that the material at 833 K, below the first transition, behaves as a normal crystalline solid with no hint of line broadening. At 923 K, above the upper transition, it behaves as a liquid, with no hint of elastic scattering, although at least two Lorentzian functions appear necessary to fit the detailed quasielastic spectra. The data at 903 K, intermediate between the two transitions, are characterized by a superposition of elastic and broadened quasielastic scattering which can be satisfactorily fitted with a  $\delta$  function and single Lorentzian function, each broadened with the instrumental resolution as given by the vanadium measurement.

Figure 4 shows the  $Q$  variation of the intensities of the fitted functions for the four runs in the intermediate phase. It is seen that the quasielastic intensity has a small peak at  $Q = 0.90 \text{ \AA}^{-1}$ , slightly below the  $Q$  value of the first peak in  $S(Q)$  at  $0.97 \text{ \AA}^{-1}$ , and starts to rise again at  $1.3 \text{ \AA}^{-1}$ , comprising most of the strength of the second peak in  $S(Q)$ . The elastic intensity accounts for most of the strength of the first peak in  $S(Q)$  with small,

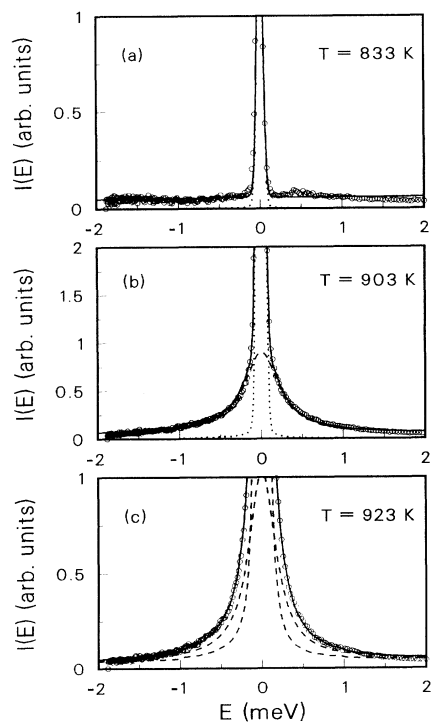


FIG. 3. Quasielastic neutron spectra of CsPb for  $41.7^\circ$  scattering angle at (a) 833 K, (b) 903 K, and (c) 923 K: data (circles), fitted  $\delta$  functions (dotted lines), Lorentzians (dashed lines), and total scattering (solid lines).

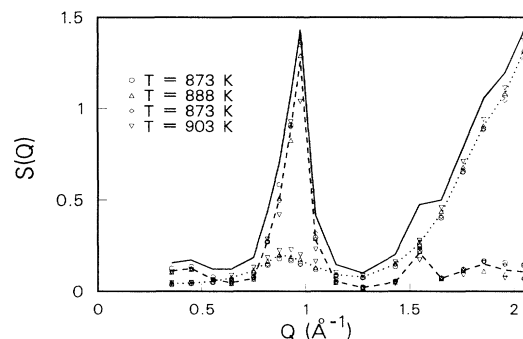


FIG. 4. Integrated intensity of  $\delta$  functions and Lorentzian functions, fitted to quasielastic spectra, and total intensities as a function of wave vector  $Q$ . The points represent data from four separate runs and the lines connect the averaged values for the  $\delta$  functions (dashed), Lorentzian functions (dotted), and total scattering (solid).

but significant, values elsewhere. The general form of these data is strongly suggestive of molecular reorientations and supports the identification of the intermediate phase as a plastic crystal.

To confirm this interpretation and identify the nature of the reorienting units and the geometry of the reorientations, a detailed dynamical model is required. The structure factor for coherent scattering from an assembly of structural units is given by<sup>12</sup>

$$S(Q) = f_1(Q) + f_2(Q)[S_c(Q) - 1], \quad (1)$$

where  $f_1(Q)$  is the form factor of the unit,  $f_2(Q)$  is another form factor expressing the correlation between two distinct units, and  $S_c(Q)$  is the structure factor describing the arrangement of the centers of the units. For the present study, we assume that the reorientations

$$\left(0, -\frac{a}{4}, \frac{c}{8}\right), \left(0, \frac{a}{4}, -\frac{c}{8}\right), \left(0, \frac{a}{4}, \frac{3c}{8}\right), \left(0, -\frac{a}{4}, -\frac{3c}{8}\right),$$

in the body-centered tetragonal unit cell. The relative positions of the Pb atoms in the four units are given by

$$\begin{pmatrix} u & v & w \\ v & -u & -w \\ -v & u & -w \\ -u & -v & w \end{pmatrix}, \begin{pmatrix} -u & -v & -w \\ -v & u & w \\ v & -u & w \\ u & v & -w \end{pmatrix}, \begin{pmatrix} v & u & w \\ u & -v & -w \\ -u & v & -w \\ -v & -u & w \end{pmatrix}, \begin{pmatrix} -v & -u & -w \\ -u & v & w \\ u & -v & w \\ v & u & -w \end{pmatrix}, \quad (2)$$

with  $u=0.1096a$ ,  $v=0.0610a$ , and  $w=0.0547c$ .<sup>1</sup> The relative Cs atom positions have the same form with  $u=-a/4$ ,  $v=-0.1424a$ , and  $w=-c/8$ . The four orientations in Eq. (2) can be derived from one another by rotation by angles of  $90^\circ$ ,  $90^\circ - 2\alpha$ , and  $2\alpha$  about the [001] axis. The angle  $\alpha = \tan^{-1}(v/u)$  has values of  $29.10^\circ$  for the Pb atoms and  $29.67^\circ$  for the Cs atoms, so the  $\text{Cs}_4\text{Pb}_4$  units can be considered to a good approximation to rotate as rigid units.

For the intermediate phase of  $\text{CsPb}$  the  $\text{Cs}_4\text{Pb}_4$  units are postulated to undergo stochastic jumps between the four orientations given in Eq. (2). The probability of occupying orientation  $j$  satisfies the rate equation

$$\dot{p}_j(t) = \frac{1}{\tau_1} p_{j-}(t) - \left( \frac{1}{\tau_1} + \frac{1}{\tau_2} \right) p_j(t) + \frac{1}{\tau_2} p_{j+}(t), \quad (3)$$

where  $\tau_1^{-1}$  and  $\tau_2^{-1}$  are the jump rate probabilities for reorientations to the nearest orientation  $j-$  (reorientation by  $90^\circ - 2\alpha$ ) and next-nearest orientation  $j+$  (reorientation by  $2\alpha$ ), respectively. Solutions of the four coupled rate equations have the form<sup>14</sup>

$$p_j(t) = \sum_k a_{jk} \exp(-\omega_k t). \quad (4)$$

The values of  $a_{jk}$  and  $\omega_k$  satisfying the initial condition that the unit is in orientation  $j=1$  at time  $t=0$  are given in Table I.

The coherent-scattering function for scattering from a single structural unit is given, without loss of generality,

TABLE I. Solutions of the rate equations for jumps between four nonequivalent orientations.

$k$	$\omega_k$	$a_{jk}, j=1, \dots, 4$			
1	0	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
2	$2\tau_2^{-1}a$	$\frac{1}{4}$	$-\frac{1}{4}$	$\frac{1}{4}$	$-\frac{1}{4}$
3	$2\tau_1^{-1}a$	$\frac{1}{4}$	$-\frac{1}{4}$	$-\frac{1}{4}$	$\frac{1}{4}$
4	$2(\tau_1^{-1} + \tau_2^{-1})$	$\frac{1}{4}$	$\frac{1}{4}$	$-\frac{1}{4}$	$-\frac{1}{4}$

<sup>a</sup> $\tau_1^{-1}$  and  $\tau_2^{-1}$  are jump rate probabilities for reorientation to the nearest and next-nearest orientations, respectively.

of each unit are uncorrelated, so the quasielastic scattering is confined to the first term of Eq. (1).

The room-temperature crystal structure of  $\text{CsPb}$  is analogous to that of  $\text{NaPb}$ .<sup>13</sup> It consists of  $\text{Cs}_4\text{Pb}_4$  structural units centered at sites

by

$$S_1(Q, \omega) = \sum_{jk} a_{jk} \rho_1(Q) \rho_j(Q) \left( \frac{\omega_k/\pi}{\omega^2 + \omega_k^2} \right), \quad (5)$$

where

$$\rho_j(Q) = \left\langle \frac{1}{b^2} \right\rangle \sum_{n=1}^N \bar{b}_n \exp(i\mathbf{Q} \cdot \mathbf{r}_n), \quad (6)$$

summed over the  $N$  atoms in the structural unit, is the scattering length density for orientation  $j$ , and the right-hand side of Eq. (5) is averaged over all orientations. The term  $k=1$  in Eq. (5), with  $\omega_1=0$ , corresponds to elastic scattering, while the three remaining terms give rise to quasielastic scattering. Integration of Eq. (5) over  $\omega$  gives  $\int_{-\infty}^{\infty} S_1(Q, \omega) d\omega = f_1(Q)$ , the first term of Eq. (1), as required.

Figure 5 shows the integrated intensities for quasielastic and elastic scattering, calculated from this model, compared with the experimental data. The model reproduces all the qualitative features of the data, including the first peak in the quasielastic intensity at  $Q=0.9 \text{ \AA}^{-1}$ . The agreement can be considered satisfactory, especially since there are no adjustable parameters appearing in the calculated intensity. The first peak in the quasielastic intensity is a little lower than the measured one, indicating that orientational correlations between distinct units are making a small but significant contribution to the quasielastic scattering, neglected in the

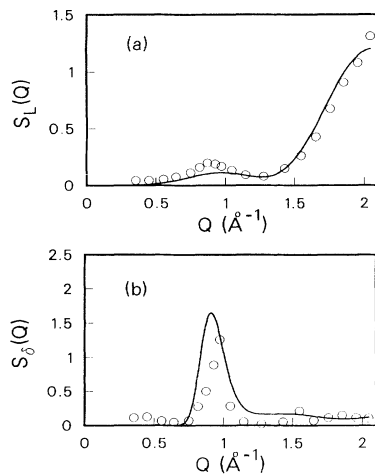


FIG. 5. Measured intensities (circles) of (a) Lorentzian and (b)  $\delta$ -function peaks, compared with intensities calculated from the model (solid lines).

simple model discussed here. The energy widths of the quasielastic peaks are approximately 0.35 meV, consistent with the present model for jump times  $\tau_1 \sim \tau_2 \sim 8$  psec.

Calculations have also been made for different structural units, e.g.,  $\text{Pb}_4^{4-}$ , and different types of reorientation, for example, about the threefold axis of the tetrahedron ( $u, v, w$ ). For *coherent* quasielastic scattering, the results are strongly dependent on the choice of structural unit and reorientation geometry, unlike the more familiar case of incoherent quasielastic scattering. In particular, omission of the Cs atoms from the structural unit makes it impossible to reproduce the first peak in the quasielastic intensity at  $Q = 0.9 \text{ \AA}^{-1}$ . Also rotational diffusion, as opposed to discrete jump reorientations, does not lead to quasielastic scattering in the coherent case and can be ruled out of the dynamical picture.

Finally, we can now calculate  $S(Q)$  for the intermediate phase from Eq. (1) and compare with the diffraction data of Fig. 2. For the comparison, we have broadened the calculated data with a Gaussian of width  $\Delta Q = 0.1 Q$  to obtain the solid line shown in Fig. 2. The agreement is seen to be excellent. This first peak is now seen to be a broadened Bragg peak, arising from two close reflections with plane spacing  $d \sim 6 \text{ \AA}$ . The remaining Bragg reflections are attenuated by the form factor  $f_2(Q)$ , and by the increased symmetry compared with the room-temperature phase, arising from the randomization of the orientations on a time-average basis.

This study has led to the following conclusions.

(1) Melting in CsPb takes place in two stages, the first to a state in which the structural units are translationally ordered but undergoing rapid jump reorientations, and the second to a true liquid in which the units are posi-

tionally disordered as well. To our knowledge this is the first observation of a plastic-crystal phase in a metal alloy.

(2) The structural unit involved is  $\text{Cs}_4\text{Pb}_4$ ; i.e., the Cs atoms are participating in the reorientations. This is consistent with the structural data in both low-temperature solid and liquid. In the latter case, inclusion of the Cs atoms in the structural unit in a model based on the random packing of structural units gives better agreement with the diffraction data.<sup>1</sup>

(3) *Coherent* quasielastic scattering provides a powerful experimental technique for studying the reorientations of molecules or structural units, being considerably more sensitive than the more familiar case of incoherent scattering for identifying the type of structural unit and reorientations involved.

We are grateful to R. Kleb for the elegant design of the sample container, the staff of the Institut Laue-Langevin for making the experiments possible, and Dr. A. J. Dianoux, Dr. J. M. Rowe, and Professor J. Woods Halley for helpful discussions. This work was performed under the auspices of the U.S. Department of Energy, Division of Materials Sciences, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

<sup>(a)</sup>On leave from the Solid State Physics Laboratory, University of Groningen, Groningen, The Netherlands.

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