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Pressure-induced suppression of the Peierls distortion of liquid As and GeX (X=S,Se,Te)

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The terminology "Peierls distortion (PD)" has been widely accepted in disordered systems ever since the discovery of PD in liquid As [R. Bellissent *et al.*, Phys. Rev. Lett. **59**, 661 (1987)]. It has not been clarified, however, to what extent the PD in liquids mirrors the PD in crystals. Here we report the observation on the pressure-induced suppression of PD in liquid As and liquid GeX (X=S,Se,Te), by which we clarified the qualitative differences as well as similarities between the PD of liquid and crystalline systems. By the appearance of prepeak that accompanies PD, we show that the intermediate-range order is related to the "Peierls distortion" in liquids, just as the Peierls distortion doubles the periodicity in one-dimensional lattice model.

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Peierls distortion[1] is a simple and widely accepted concept for crystalline systems, which was extended to liquid systems in 1987.[2] The terminology "Peierls distortion" is now widely accepted and used in various disordered systems.[3–6] However, it has not been clear to what extent "Peierls distortion" in liquids mirrors that in crystals. In this work we have observed a pressure-induced suppression of "Peierls distortion" in liquid for the most typical system liquid As.

We found that intermediate-range order is caused by the distortion, which reminds us the doubling of the periodicity in the Peierls distortion scenario in the crystalline one-dimensional chain model.[1] This result is an example that reveres the long-held stance: so far, for liquid systems, it had not been believed that there is a relationship between intermediate-range order and "Peierls distortion" in liquids. Our results thus show that "Peierls distortion" in liquid causes a prepeak, i.e., intermediate-range order.

We also investigated *IV-VI* compounds GeX (X=S,Se,Te) and found universal properties of pressure-induced suppression of Peierls distortion in these liquids including liquid As. We report two qualitative differences between liquid and crystalline "Peierls distortion:" (1) the bond length expands in the process of suppressing the Peierls distortion. This is in good contrast to the crystalline systems where the bond shorten in the same process.[7] (2) There is no difference between "A7-type" and "A17-type" liquids from the viewpoint of pressure sequences, which is in good contrast to the different pressure sequences between A7 crystals (A7 and GeTe) and A17 crystals (GeS and GeSe).

Here we start from giving a brief summary of the Peierls distortion scenario in crystalline group-V elements: for As, Sb, and Bi, the valence-electronic configuration is s^2p^3 and the two s electrons are in a deep level and do not participate in the bonding. Since the directions of the distribution of 3 p-electrons are expected to be orthogonal (p_x, p_y, p_z), the most stable structure can be expected to be a simple cubic (SC) structure. However, the SC structure is known to have a Peierls instability[8] which results in an A7 structure and this is thus the room temperature allotrope for As, Sb and Bi (and P under pressure). Peierls distortion takes place along the (1 1 1) direction (see A7 structure in Fig. 1), splitting the six nearest neighbors (NNs) of the SC structure into three NNs and three next NNs. Also, the bond angle distorts from 90° and becomes larger than 90° in the A7 structure.

Bellissent *et al.*[2] proposed that the structure of liquid (l-) As is closely related to the crystalline A7 structure,[9] and this conclusion was also supported by theoretical studies.[10,11] They also suggested that this structure is the consequence of the same Peierls distortion which leads to the A7 structure for the crystalline state of group-V elements. "Peierls distortion" in disordered systems is now a widely accepted terminology; for example, l-As,[2] l-P under pressure,[12] liquid *IV-VI* compounds/clusters,[13] l-Na,[3] liquid transition metals,[4] and l-GeSbTe alloys[5] are regarded as "Peierls-distorted" liquids. The criteria of "Peierls distortion in liquid" are listed in Ref. 14: (1) six NNs of the SC splits into three NNs and three next NNs, and (2) the bond angle becomes larger than 90° in the "Peierls-distorted" liquids.

To clarify the nature of "Peierls distortion" in liquids, we investigated the structure of l-As under pressure. It is well known that Peierls-distorted crystals recover a higher symmetry under pressure. For the most known example, an abrupt transition from A7 to the SC structure occurs at 25 GPa for crystalline As.[15]

We also investigated l-GeX (X=S,Se,Te) to clarify the general properties of "Peierls distortion" in liquids. To date, only two types of Peierls distortion are known for group-V and isomorphic (average-valence-V) IV-VI crystalline compounds: As shown in Fig. 1, under ambient conditions, As and GeTe have the A7 crystal structure, whereas GeS and GeSe takes the A17-type structure. Importantly, A17 (or B16, if there are two types of atoms) can also be regarded as a Peierls distortion of the SC (or B1, if two types) structure.[16] The reason is that Peierls distortion is a short-long alternation of bonds, i.e., pairing, and there are several ways in which the pairing may occur (see Fig. 1). Under compression, A7-type crystals transform into the SC structure. On the other hand, A17-type crystals do not[17] because of the shift of every other layer shown in Fig. 1. In short, the crystalline pressure sequences are different between A7-type and A17-type Peierls-distorted structures.[17] Then, how is the pressure sequences for "Peierls-distorted" liquids? On melting, the structure of these four liquids, l-As and l-GeX, has previ-

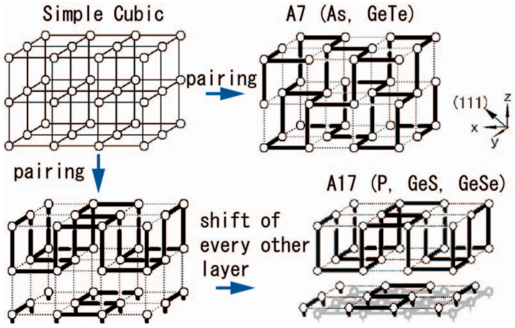

FIG. 1. (Color) Schematic figures of SC, A7, and A17 structures. Gray symbols shown in A17 structure are the original positions of atoms before the shift of every other layer.

ously been shown to have “Peierls distortion.”[2,18] We thus report the observation of pressure-induced suppression of “Peierls distortion” for these liquids and clarify the nature of “Peierls distortion” in liquids by comparison of the structural changes in liquids to that in crystalline pressure sequences.

Synchrotron x-ray diffraction measurements were performed with a multianvil high-pressure apparatus using an energy-dispersive method. We used the single-stage high-pressure apparatus MAX80 installed at the beamline NE5C in PF-AR (Photon Factory—advanced ring for pulse x rays) at KEK, Japan. Above 10 GPa, we used the Kawai-type double-stage high-pressure apparatus SPEED1500 installed at BL04B1 in SPring-8, Japan. Measurements were done at temperatures approximately 50 K above the melting point at each pressure, except for the lowest pressure measurement for *l*-As at 1 GPa, which was taken at just above the melting point to avoid the melting of the NaCl sample cell. The temperature and pressure ranges are from 850 to 1050 °C, from 1 to 17 GPa for As, from 750 to 1250 °C, from 1 to 7.5 GPa for GeS, from 800 to 1100 °C, from 0.5 to 15 GPa for GeSe, and from 850 to 1100 °C, from 0.6 to 8.5 GPa for GeTe. Details of the methods of measurements and analysis are given in Refs. 19 and 20 and preliminary results in Refs. 21 and 22.

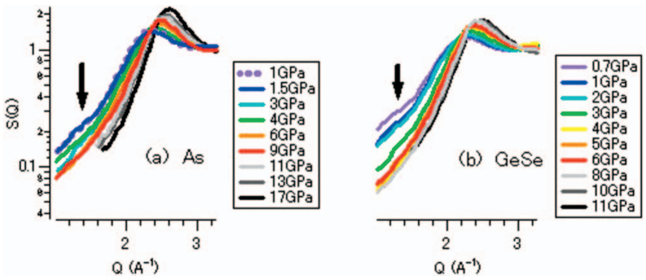

FIG. 2. (Color) $S(Q)$ at high pressures in the low Q ranges for (a) *l*-As and (b) *l*-GeSe in single logarithmic plot. The arrows indicate the prepeak. See Refs. 2 and 18 for the sharper prepeaks in lower pressures for *l*-As and *l*-GeSe, respectively.

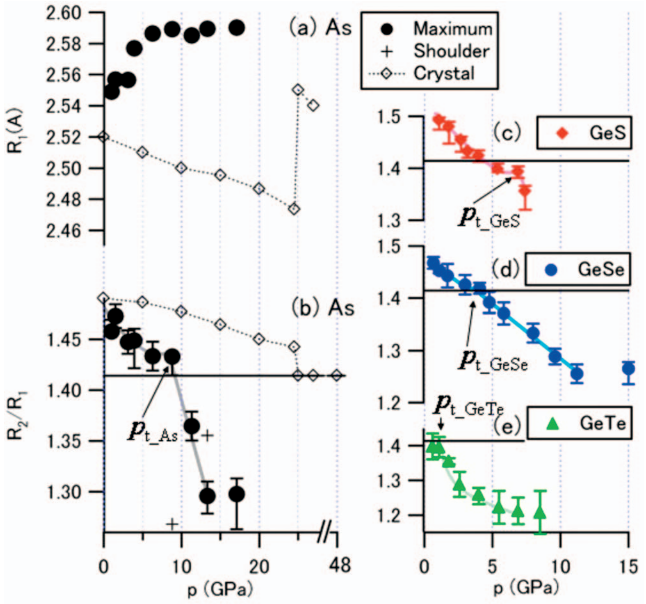

FIG. 3. (Color) The pressure dependence for the first peak position (a), and the ratio of the second peak position to the first (R_2/R_1) (b), of $g(r)$ for *l*-As. For comparison, the pressure dependence of corresponding values in crystalline phase are also shown in (a) and (b) by open diamonds. Here, R_1 and R_2 for the crystalline state are the distance of the intralayer 1st and 2nd NNs in A7 phase, respectively. Those crystalline values were calculated by Refs. 7 and 23. (c)–(e) show R_2/R_1 for three liquid compounds. The horizontal lines in (b)–(e) show $R_2/R_1=\sqrt{2}$, which is the value for SC structure. The curves behind the symbols are guide for the eyes.

As shown in Fig. 2(a), we observed the disappearance of the “prepeak” with increasing pressure. We note that we reported $S(Q)$ for wider Q range in Refs. 21 and 22. Although the peak height is small, this prepeak has been more clearly and sharply observed near the ambient pressure in Ref. 2, and the existence of a prepeak in liquids or glasses indicates a nonrandom intermediate-range order,[24] which is very rarely seen in *elemental* liquids. The observed disappearance of the prepeak may suggest a change from two-dimensional to three-dimensional structure, as have been discussed for a liquid GeSe alloy in Ref. 25. Some theoretical works for *l*-As and *l*-P (Refs. 10 and 12) and a force-constant calculation for crystalline (*c*-) As (Ref. 26) also support the layerlike (A7-type) two-dimensional structure of *l*-As in low pressures. With suppressing the “Peierls distortion,” the local orientational symmetry will be recovered, i.e., from lower 2+1 (2 covalent and 1 van-der-Waals-like bonds) to three-dimensional (three metallic bonds) isotropic symmetry. We note in passing that, for a lighter group-V liquid P, the low-pressure form of *l*-P_4 is known to show a sharp prepeak due to the correlation between the P_4 molecules,[27,28] and this persists into the high-pressure polymeric phase.[29] However, it has been clearly denied that As_4 molecules remain to cause As_4-As_4 correlation in *l*-As.[10,28,30] The shape of the structure factor $S(Q)$ or the pair distribution function $g(r)$ also deny the possibility.

Importantly, the disappearance of the prepeak accompanied by the suppression of “Peierls distortion” was also observed for *l*-GeSe, as shown in Fig. 2(b). For *l*-GeS, we observed small but the same tendency, whereas we did not observe any remnant of prepeak for *l*-GeTe. The absence of prepeak for *l*-GeTe may be due to that the structure is already three-dimensional and Peierls distortion is nearly suppressed in low pressures. Here the important point is that, at ambient pressure, a clear prepeak was observed even for *l*-GeTe,[18] and it has been shown that *l*-GeTe is a *slightly* "Peierls-distorted" liquid at ambient pressure.[13]

It is interesting that "pressure-induced suppression of Peierls distortion" was found to generally suppress the intermediate-range order in liquids, for the elemental liquid as well as compounds. The disappearance of the prepeak on the pathway of suppressing the distortion reminds us how a one-dimensional periodic metal results in a Peierls-distorted semiconductor: When a Peierls instability doubles a period in a one-dimensional metallic lattice whose electronic structure is half-filled, a new Bragg peak appears at low Q range due to the doubling of the periodicity. This mechanism may be more or less similar to what is happening in the Peierls-distorted liquids; i.e., Peierls-distorted liquids are now found to show prepeak at low Q and have been known to be semiconducting,[2,31] whereas the not-distorted liquids are expected to be metallic.[10]

Furthermore, given that a intermediate-range order was indeed observed in "distorted" liquid, "Peierls" distortion can be regarded as a rather natural terminology rather than "Jahn-Teller" distortion, because the longer-range periodicity is the concept naturally born out from the doubling of the periodicity in the original Peierls distortion scenario in the one-dimensional lattice model, and also because of the electronic scenario mentioned above. This suggestion is supported by the sharper and clearer prepeak in lower pressures,[2,18] which can be regarded to reflect the intermediate-range order or, basically, longer "periodicity" because a peak in reciprocal space should be due to a somewhat periodic-type structure. Our result thus give a support to the terminology "Peierls distortion" in liquids, although there had been believed to be no difference between "Peierls" and "Jahn-Teller" distortion in liquids, as stated in Refs. 9 and 14.

Second, we found a systematic structural change for all four liquids: R_2/R_1 asymptotically approaches $\sqrt{2}$ with pressure, and interestingly, the contraction changes when $R_2/R_1 \sim \sqrt{2}$, as shown in Figs. 3(b)–3(e). Here, R_1 and R_2 are the first and the second peak positions in $g(r)$, respectively, and thus the results suggest that the bond angle is approaching 90° just as is observed in the crystalline SC material during the process of the suppression of the Peierls distortion. However, for As, whereas the SC structure is stable to 48 GPa in the crystal,[32] in the liquid is clear that the structure changes largely above 10 GPa to a more densely packed structure. The reason for this difference between liquid and crystal is that crystal responds to pressure by reducing its bond length, keeping the constant bond angle, but in the liquid it is energetically more favorable to change the bond angle, keeping nearly the same bond length (with small expansion) with pressure, as can be seen in Figs. 3(a) and 3(b).

For the compounds, the important result is that we observed "pressure-induced suppression of Peierls distortion" (or the appearance of denser structure) for all three liquid compounds in relatively low pressures p_t shown in Figs. 3(c)–3(e). The point here is $p_t \leq 10$ GPa, in spite of that the crystalline A17-type compounds (*c*-GeS and *c*-GeSe) have shown no phase transition up to 34 and 82 GPa, respectively, which is in good contrast to the A7-type crystals (GeTe and As) that transform from A7 to SC at 3 and 25 GPa, respectively.[17] The large pressure required for A17-type crystals is due to the shift of every other layer shown in Fig. 1 which is crucial for the crystalline systems but not for liquid systems. We thus conclude that we found p_t in systematic order in liquid compounds, $p_{t(\mathrm{GeS})} > p_{t(\mathrm{GeSe})} > p_{t(\mathrm{GeTe})}$, which is in good contrast to the *qualitative* difference in the crystalline structure, i.e., the difference between A7-type and A17-type pressure sequences in crystals.

In summary, we reported observations of pressure-induced suppression of "Peierls distortion" in liquid systems and found a similarity between "Peierls distortion" of liquid and crystalline systems: "Peierls distortion" in liquids was found to cause intermediate-range order, which resembles the doubling of the period in crystalline one-dimensional chain model. In this sense, the distortion in liquid As could be called "Peierls" distortion rather than "Jahn-Teller" distortion that does not require longer periodicity, although these two types of distortion have been thought to be the same in liquid systems ever since Refs. 2 and 9. We also found two qualitative differences between the "Peierls distortion" in liquid and crystalline systems: (1) the bond length expands during the suppression of the "Peierls distortion" in *l*-As, which is contrast to the bond contraction in the same process in crystalline As.[7] (2) The structure of *l*-As and all *l*-Ge*X* show the same pressure dependences, i.e., the "Peierls distortion" was found to be the same for these liquids, in contrast to the different crystalline structure (and thus different pressure sequences and different type of Peierls distortion) between A7 (stable for As and GeTe) and A17 (GeS and GeSe). These differences between liquid and crystalline systems can be traced back to the absence/presence of the periodicity: (1) in liquid "SC-like" structure, the bond angle need not to be strictly conserved. In the crystalline SC system, on the other hand, the bond angle is fixed at 90°. Thus, in liquids, structure tend to respond to the pressure by mainly changing the bond *angle*, whereas, in crystals, by changing the bond *length*. (2) There is a well-defined difference between crystallographic symmetry of A7 and A17. On the other hand, in liquids, these are the same in respect of their short-range order. Their structural pressure dependences were thus found to be the same in the liquid state.

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