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Relationship between Peierls Distortion and Medium-Range Order in Liquid Group-V elements and Liquid Group-IV-VI Compounds

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Abstract. We have done energy-dispersive x-ray diffraction for liquid As, Sb, GeS, GeSe, GeTe, and found that there is a relationship between medium-range order (MRO) and the Peierls distortion (or charge-density-wave structure) in these liquids. The prepeak disappears when the Peierls distortion is suppressed. In this paper we explain the relationship between MRO and Peierls distortion in liquids by a tentative assumption that the prepeak could be a remnant of satellite peaks in the Peierls-distorted crystals.

1. Introduction

Arsenic (As) is known to be a typical example that shows an A7 structure due to the Peierls instability. [1] Peierls distortion (or charge-density wave structure) is originally suggested by use of an one-dimensional chain model shown in figure 1.[2] When the one-dimensional lattice [figure 1 (a)] is electronically half-filled as shown in (c), the system will show a Peierls instability, which leads to more energetically favourable structure (due to the change of the Fermi level) shown in (b). Since the valence-electronic configuration of group-V elements is s^2p^3 and the s electrons are deep in level and basically do not participate in the bonding, simple cubic (SC) structure [figure 1 (e)] could be thought of as an apparent stable structure because of the orthogonal nature of p_x , p_y , and p_z electronic orbital. However, the Peierls distortion is thought to take place in x, y, and z directions, and the actual structure results in the A7 structure shown in (f), because electronic structure can be regarded as effectively that of three almost independent one-dimensional systems.[1] One can easily see that the short-long alternation is taking place in the three directions, x, y, z in (f).

There is a well-known pressure-induced phase transition in crystalline As from A7 structure to SC structure.[3]. In liquid state, we have found that the same kind of pressure-induced suppression of the Peierls distortion takes place for liquid As as well as for liquid GeX (X=S, Se, Ge) compounds.[4] In this paper we shall explain the relationship between the medium-range order and the Peierls distortion in liquids from the ground up.

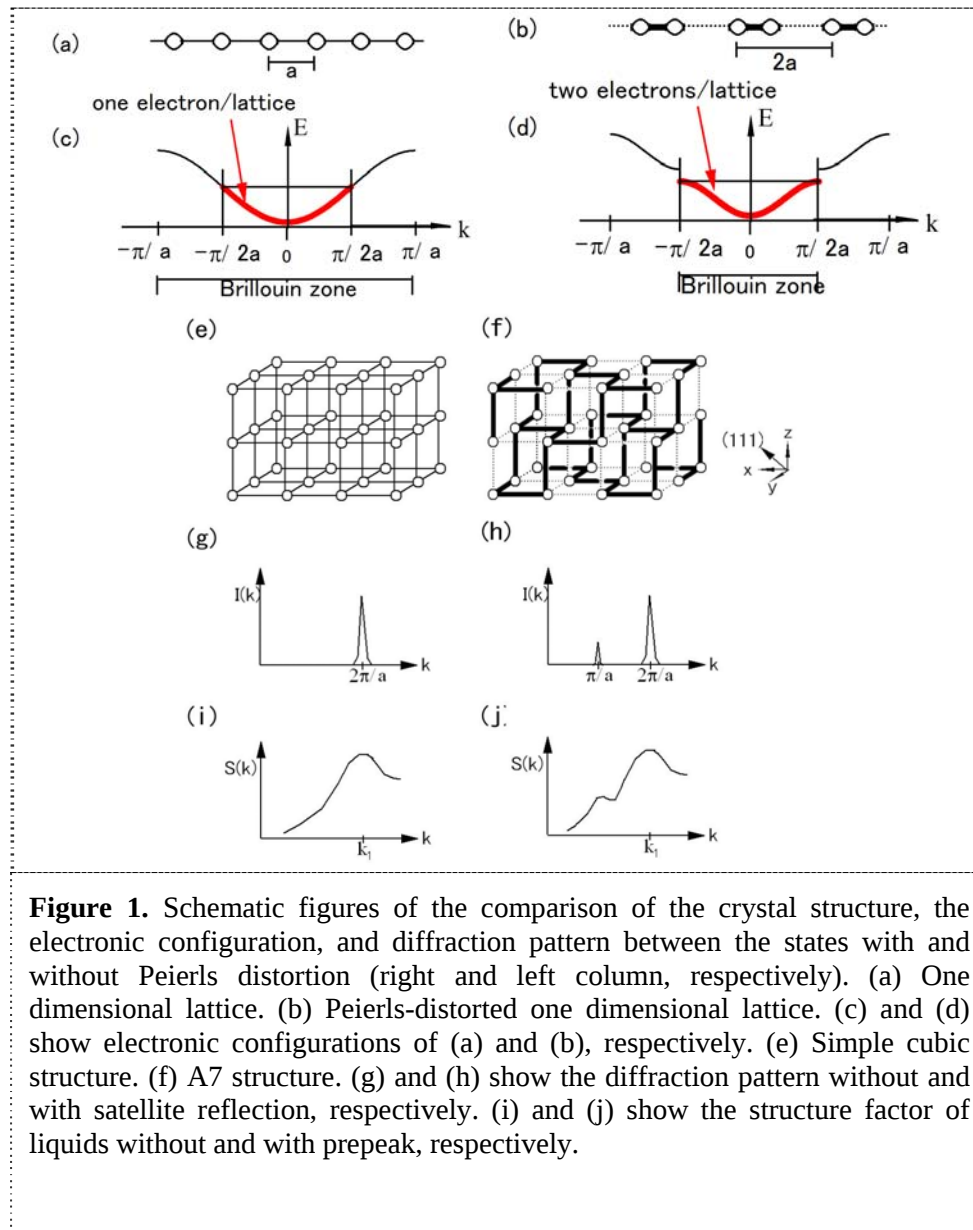


Figure 1. Schematic figures of the comparison of the crystal structure, the electronic configuration, and diffraction pattern between the states with and without Peierls distortion (right and left column, respectively). (a) One dimensional lattice. (b) Peierls-distorted one dimensional lattice. (c) and (d) show electronic configurations of (a) and (b), respectively. (e) Simple cubic structure. (f) A7 structure. (g) and (h) show the diffraction pattern without and with satellite reflection, respectively. (i) and (j) show the structure factor of liquids without and with prepeak, respectively.

2. Experimental

We have carried out energy-dispersive x-ray diffraction experiments at MAX80 installed at the beam line NE5C at PF-AR, KEK, Japan and SPEED1500 installed at BL04B1 at SPring-8, Japan. The measurements are done at about 50K above the melting point at each pressure for each sample, except for the lowest pressure 1GPa for liquid As, which was measured just above the melting point to avoid the melting of the NaCl sample cell. Details of the methods of measurements and analysis are given in Refs. 5 and 6, preliminary results in Refs. 7 and 8, and main results in Ref. 4.

3. Results

Figure 2 shows the low- k part of the pressure dependence of the structure factor $S(k)$ for liquid As. Here k denotes the wave number. We note that the pressure dependence of wider region of $S(k)$ up to $10\text{\AA}^{-1}$ have been published in Ref. 7, and reliable data was taken up to at least $18.3\text{\AA}^{-1}$ for each pressure. In figure 2, we observed a prepeak in low pressures which disappears at high pressures. At

lower pressure, importantly, Bellissent *et al.* published a sharper prepeak for the same liquid As.[9] We note in passing that prepeak is rarely seen in elemental liquids and the origin of the prepeak is often related to the concentration fluctuation in liquid multi-element compounds.[10]

We also observed the same disappearance of the prepeak for liquid IV-VI compounds,[4] and at lower pressures Raty *et al.* published structure factor in which the prepeak was also observed and importantly it seems to be sharper and clearer.[11] For liquid Sb, we observed almost no prepeak, but we may say that there was some remnant. This result is consistent with the papers that suggest no Peierls distortion in liquid Sb [12] or very little distortion remains.[13]

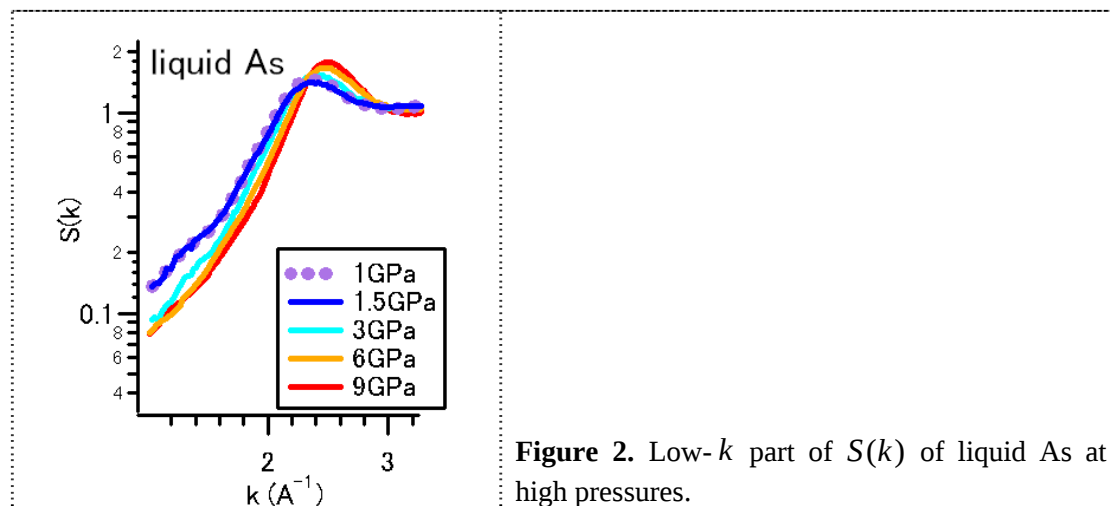


Figure 2. Low- k part of $S(k)$ of liquid As at high pressures.

4. Discussion

Here we consider the physical meaning of the prepeak. The essence of the diffraction patterns of the not-distorted and Peierls-distorted crystalline structures are schematically shown in Fig.1 (g) and (h), respectively. The simplest explanation for figure 1 (g) is shown in figure 3: The Bragg reflection is caused by the optical path difference shown in figure 3 (a). When the path difference is equal to the integral multiple of the wave length, i.e., $2a \sin \theta = n\lambda$, Bragg condition is satisfied. Here a denotes the distance of the periodicity in Fig.1 (a), 2θ is the scattering angle shown in (b), λ is the wave length of the x-ray we use in the experiment. The momentum conservation law in the scattering process is shown in figure 3 (b). Here the scattering is basically elastic, thus, $k_f = k_i$, and it follows that $k = 2k_i \sin \theta = 4\pi \sin \theta / \lambda$. The relation $2a \sin \theta = n\lambda$ above then results in the Bragg condition $k = n \cdot 2\pi / a$, which finally results in the scattering pattern in figure 1 (g). When the Peierls distortion takes place and charge-density-wave long-range order is nearly achieved, the periodic lattice distortion gives the satellite reflections around the Bragg peak as shown schematically in figure 1 (h), whose intensity, shape and width will depend on the domain size of the charge density wave.[14] In short, when the Peierls distortion takes place, the satellite reflection appears, and finally the Brillouin zone reduces down to half as shown in figure 1 (d).

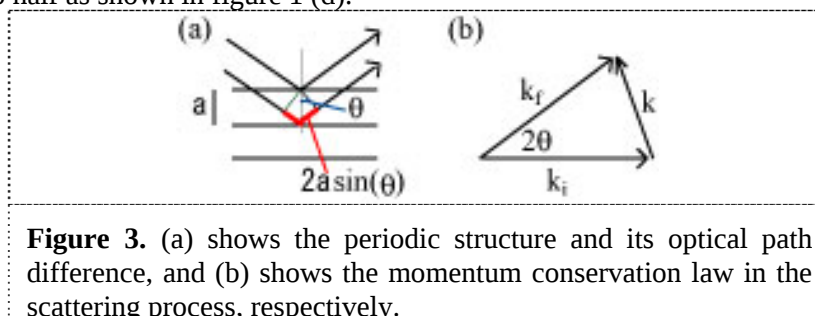


Figure 3. (a) shows the periodic structure and its optical path difference, and (b) shows the momentum conservation law in the scattering process, respectively.

In liquid state, the structure factor $S(k)$ could be regarded as a counterpart of the Bragg reflection [See figure 1 (g) and (i)]. Thus the pseudo Brillouin zone boundary is defined at $k_1/2$, where k_1 is the first peak position of $S(k)$. This concept could be naturally accepted when one reminds that the acoustic dispersion relation in liquids: The energy of the acoustic mode takes maximum at around $k_1/2$ and minimum at around k_1 . [15] In this sense, the prepeak could be regarded as a remnant of the satellite peak for the Peierls distorted crystals [See figure 1 (h) and (j)]. In general, it has been suggested that the prepeak can be regarded to define a narrower pseudo Brillouin zone and the dispersion relation of the acoustic mode follows this narrower pseudo Brillouin zone when the prepeak exist, [16] and also the de Gennes narrowing of dynamic structure factor has been suggested at the prepeak position. [17]

In figure 2, we observed the prepeak disappears when the Peierls distortion is suppressed significantly. Here the suppression of the Peierls distortion can be judged by the pressure dependence of R_2/R_1 , where R_1 and R_2 are the first and second peak positions of the pair distribution function. That is, this ratio reduces down to $\sqrt{2}$ at 9 GPa, and this result shows that the bond angle is nearly 90 degree and that the Peierls distortion is almost suppressed at this pressure. [4] Our result in figure 2 thus suggests there is a relationship between the prepeak and the Peierls distortion in liquid As. The same results for the compounds [4] also suggest the relationship. There may be a correspondence relationship between the charge-density-wave long-range order in Peierls distorted crystals and the medium-range order in Peierls distorted liquids.

Furthermore, liquid As at low pressures are thought to be semiconducting [9] and the high pressure phase metallic. [18] We may say that the "Peierls distortion" scenario seems to naturally work, regarding such electronic nature as well as the structural changes. Although this might be a too simplified suggestion, and we note that the prepeak in figure 2 is small and does not appear at $k_1/2$, we may also note that a sharper prepeak at lower pressure in Ref. 9 is observed at almost $k_1/2$ [19] and our simple suggestion could be related to the nature of the issue "Peierls distortion" in liquids.

5. Conclusion

We suggest from our diffraction measurements that there is a relationship between medium-range order and "Peierls distortion" in liquids. In this paper we suggested and explained a correspondence relation between the satellite peaks in Peierls-distorted crystals and the prepeak in Peierls-distorted liquids, as an attempt at interpretation of "Peierls distortion in liquids".

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