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To cite this version:

HAL Id: jpa-00220198
https://hal.archives-ouvertes.fr/jpa-00220198
Submitted on 1 Jan 1980

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GAMMA-RAY COMPTON SCATTERING OF GERMANIUM AND SELENIUM IN SOLID AND LIQUID STATE

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INTRODUCTION

γ-ray Compton scattering measurements have been so far successfully performed to elucidate the electronic structure of not only the solid state but also the liquid state of metals. These studies have shown that the volume change upon melting plays an important role in the modification of the Compton profile between the solid and liquid states of metals such as Li[2,3], Na[2,3], Al[4] and Ga[5].

Ge and Se have typical semiconducting properties in the solid state. In the liquid state, however, Ge is known to show a metallic character; the electrical conductivity[6] has a negative temperature coefficient and the number of carrier is estimated to be about 4 electrons per atom by Hall coefficient measurement[7]. Se takes gradual changes in various electronic properties upon melting and still remains as a semiconductor even in the liquid state[8].

The purpose of this study is to examine directly what happens in the electronic structure of Ge and Se through the solid-liquid transition by means of the Compton scattering method.

EXPERIMENTAL

Compton scattering measurements were carried out using 59.54 keV γ-rays emitted from 1 Ci $^{241}$Am annular source. The γ-ray spectrum scattered by the sample through an scattering angle of 165° was measured with a pure Ge solid state detector. The resolution of the detector at 59.54 keV was 340 eV (FWHM) in the energy scale, or 0.53 a.u. in the momentum scale.

The specimen Ge of 99.99 % purity was contained in the carbon vessel of 26 mm inner diameter and 3.5 mm depth which was located in a vacuum chamber(5x10^{-6} Torr) with an aluminum window(0.1 mm in thickness). Details of the experimental set up used have been described in the previous papers[2,3]. Both of the opening sides of the carbon vessel were sealed with thin carbon foils of 0.17 mm in thickness.

Firstly, the Compton profile of Ge was measured for the liquid state(at 970°C) and then for the solid state(at 24°C) solidified in-situ in the vessel without alteration of the initial arrangement of the detector and the sample. The measuring duration required about 10 days to accumulate 39,000 counts at the Compton peak.

The same experimental techniques were applied to measure the Compton profiles of Se in the liquid and solid(trigonal and amorphous) states. In these cases, however, the stainless steel vessel of 26 mm inner diameter and 2 mm depth was used instead of the carbon vessel. The opening sides of the stainless steel vessel were sealed with stainless steel foils of 5 μm in thickness. The measurement of the Compton profiles of Se was performed under 1 atmosphere of pure argon gas to suppress the vaporization from liquid Se(at 277°C). Trigonal Se crystal was obtained by in-situ annealing the solidified specimen at 200°C for 36 hours. Amorphous solid of Se was prepared by quenching molten Se into ice water. The Compton profile of amorphous Se was measured without using the vessel in the vacuum chamber(5x10^{-6} Torr) mentioned above. Trigonal and
amorphous phases of Sr identified by X-ray diffraction.

RESULTS AND DISCUSSION
The Compton profile $J(q)$ was obtained by the generalized least squares method of the Fourier analysis after subtracting background contributions due to the carbon (or stainless steel) foils, gas-atmosphere and cosmic rays, and performing the multiple scattering correction and various energy dependent corrections. Details of the present data processing procedures have been fully described elsewhere[3].

Fig.1 shows the differential Compton profile of Ge between the liquid and solid state, $\Delta J(q)$, defined as follows,

$$\Delta J(q) = J_{\text{liq}}(q) - J_{\text{sol}}(q). \quad (1)$$

The $J(q)$ of Ge is normalized to $24.807/2$ over the range from $q=0.0$ to 5.0 a.u. using the free atom wave functions by Clementi[9]. The contribution of $1s^2$ electrons is neglected in this normalization value because the binding effect appears at $q=0.1$ a.u. in the Compton profile. Two experimental runs were done for liquid Ge to confirm the reliability of data. As shown in Fig.1, the experimental $\Delta J(q)$ of Ge has a large negative value in the range of $|q|<1.5$ a.u. and shows a maximum around $q=2.0$ a.u. and then approaches gradually to zero. The dotted line in Fig.1 shows the theoretical $\Delta J(q)$ for Ge calculated by assuming that four valence electrons per atom behave as the free electron in the liquid state as well as in the solid state. The theoretical $\Delta J(q)$ thus calculated is very far from the experimental one. This discrepancy is in contrast to the nice agreement between the experimental and the theoretical $\Delta J(q)$ based upon the free electron model for Li[3], Na[3], Al[4] and Ga[5].

Hence, the characteristic behavior of the experimental $\Delta J(q)$ as shown in Fig.1 must be ascribed to the other effects which originate from the semiconductor-metal transition in Ge upon melting. In order to verify this conjecture, we try to construct a model $\Delta J(q)$ based upon the

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Fig.1 Differential Compton profiles of Ge between the liquid and solid state, $\Delta J(q) = J_{\text{liq}}(q) - J_{\text{sol}}(q)$. The solid and broken curves indicate the experimental. The bars show the statistical uncertainties. The dotted curve indicates the theoretical $\Delta J(q)$ calculated from the free electron model.

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Fig.2 Comparison of the differential Compton profiles for Ge between the experiment (solid curve) and the theoretical. The broken curve denotes the differential Compton profile between $4s^14p^{2.5}$ configuration and $4s^14p^3$ configuration using Clementi's free atom wave functions[9]. The dotted curve denotes the difference between $4s0.54p^{3.5}$ and $4s^14p^3$ configurations.
LCAO hybridization. The band structure of solid Ge is naturally believed to consist of the covalent \(sp^3\) hybridization of \(4s\) and \(4p\)-atomic orbitals. We assume here that the \(4s4p^2\) configuration in solid Ge is modified upon melting into the \(4s^24p^3\) configurations in liquid Ge. For example, the theoretical \(\Delta J(q)\) in cases of \(4s^24p^2\) and \(4s^14p^3\) electronic configurations for liquid Ge are shown in Fig.2 together with the experimental one. The former model which describes the electron transfer from the \(p\)-like state to the \(s\)-like state is likely to represent the feature of the experimental \(\Delta J(q)\) except for around \(q = 0\) a.u. The discrepancy near \(q = 0\) a.u. can be reduced by taking into account the volume effect as shown in Fig.1. It is concluded that \(s\)-like electrons increase while \(p\)-like electrons decrease in liquid Ge upon melting and that the metallic character of liquid Ge comes out from the electron transfer from the \(p\)-like state to the \(s\)-like state accompanied by melting.

Fig.3 shows the differential Compton profiles \(\Delta J(q)\) between various Se phases. Each Compton profile of Se is normalized to 26.054/2 over the range from \(q = 0\) to 5.0 a.u., using Clementi's free atom wave functions[9]. The contribution from \(1s^2\) electrons is omitted in the normalization value because \(1s^2\) electrons of Se can not be excited in the range greater than \(q = -2.4\) a.u. under the present experimental condition.

The \(\Delta J(q)\) of Se between the liquid and trigonal crystal phase is the largest and the \(\Delta J(q)\) between the liquid and amorphous state is the smallest. The \(\Delta J(q)\) between the amorphous and trigonal crystal state is similar to the result observed by Bonse et al[10]. Since Se has little conduction electrons in the liquid as well as in the solid state, the characteristic behaviors in the \(\Delta J(q)\) as shown in Fig.3 is likely to reflect the variation in the chemical bonding nature of valence electrons through the transition from the trigonal crystal state to the liquid or amorphous state.

It is interesting to compare the present results with the structural data of various Se phases as shown in Table I. The bond angle(\(a\)) and intra-molecular bond length(\(d_1\)) are kept almost same values in any Se phase, while the inter-molecular atomic distance(\(d_2\)) is lengthened with decreasing mass density(\(\rho\)).

![Fig.3 Differential Compton profiles \(\Delta J(q)\) of Se between three states with statistical error bars. Open and closed circles denote the \(\Delta J(q)\) between liquid(L) and trigonal(Tr) Se and between amorphous(A) and trigonal Se, respectively. Triangles denote the \(\Delta J(q)\) between liquid and amorphous Se.](image)

According to the calculation by Joannopoulos et al[15], the charge density of \(p\)-like electrons in the inter-molecular region decreases as the inter-molecular atomic distance(\(d_2\)) increases while the \(s\)-like electrons remain relatively unchanged. This suggests that the characteristic behavior of \(\Delta J(q) > 0\) around \(q = 0\) a.u. as shown in Fig.3 may be related to some decrease in the charge density of inter-chain bonding \(p\)-like electrons in amorphous and liquid Se. This conclusion

<table>
<thead>
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<th>phase</th>
<th>(\rho) (g/cm(^3))</th>
<th>(d_1) (A)</th>
<th>(d_2) (A)</th>
<th>(a) (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trigonal</td>
<td>4.819</td>
<td>2.37</td>
<td>3.44</td>
<td>103</td>
</tr>
<tr>
<td>amorphous</td>
<td>4.205</td>
<td>2.32</td>
<td>3.72</td>
<td>104-105</td>
</tr>
<tr>
<td>liquid</td>
<td>3.912</td>
<td>2.38</td>
<td>3.75</td>
<td>103-106</td>
</tr>
</tbody>
</table>
is consistent with the previous observations by positron annihilation measurements [16,17].

Furthermore, recent theoretical studies [18-21] have shown that the Compton profile of amorphous Se deviates from that of the polycrystalline phase into that of the free atom state. This result provides the qualitative explanation for the experimental $\Delta S(q)$ of Se shown in Fig.3. These theoretical studies, however, depend upon a random distribution of atoms or one-dimensional potential arrays. Hence, it would be of interest to examine the Compton profile of amorphous or liquid Se taking into account the more realistic atomic arrangement.

References

8. see for example, Selenium, ed. Zingaro, R.A. and Cooper, W.C. (reinhold, New York) 1974; see also ref. [6].

*Vertical bars in Figs. 1 and 3 show the statistical fluctuation in total counts for $\Delta S(q)$, i.e. $\sqrt{N}$ (N: counts number) at several q values. The experimental uncertainty involved in $\Delta S(q)$ is much less than the statistical uncertainty, because a curve-smoothing procedure has been applied during the data processing as described in the text. Therefore, the characteristic behaviors of $\Delta S(q)$ in $q < 1.5$ a.u., which have been intensively discussed in this paper, are qualitatively acceptable.