PHYSICAL REVIEW B VOLUME 59, NUMBER 3 15 JANUARY 1999-I

Electronic structure study of liquid germanium based on x-ray-absorption near-edge structure spectroscopy

Chenxi Li, Kunquan Lu, and Yuren Wang
Center for Condensed Matter Physics & Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

Kozaburo Tamura, Shinya Hosokawa,* and Masanori Inui
Faculty of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739, Japan

(Received 7 July 1998)

Based on measured x-ray-absorption near-edge structure spectra of crystalline and liquid germanium (*c*-Ge and *l*-Ge), multiple-scattering simulation and density-of-states (DOS) self-consistent calculation have been carried out. By using the configurations generated with a reverse Monte Carlo simulation, the higher and narrower white line resonance relative to the solid, and the smearing of any other features *l*-Ge above the edge are reproduced and explained, and the metallic character is verified by DOS calculations. The strong white line for *l*-Ge is attributed to the high density of states in the conduction band and partially to the excitonic effect. The DOS of *l*-Ge is quite high around the Fermi level, as in a metal, while that for *c*-Ge opens a gap there. Taking the core-hole effect into account, the *p*-like partial DOS in the vicinity of the absorbing atom shows a DOS ''piling up.'' [S0163-1829(99)06303-1]

The melting of covalent semiconductors such as Si, Ge, GaSb, InSb, etc. exhibits a special phenomenon in which the covalent bond is destroyed and a semiconductor-metal transition occurs.[1–3] The density of the liquids is greater than that of the solids, and the coordination number increases to 6–7 which is, however, less than that of 10–12 found in normal liquid metals.[4–6] The phenomena have attracted considerable research interest in both technological and basic sciences. To understand the mechanism involved it is necessary to study both the atomic and electronic structures of the liquids in comparison with the solids. Some reliable results on the atomic structure have been obtained in recent years.[4] The solid-liquid transition of Ge and the local order of *l*-Ge have also been studied with x-ray diffraction and x-ray-absorption fine-structure measurements.[7–9] However, experimental studies on the electronic structure are still limited because of the practical difficulties. Here we report an electronic structure study of *l*-Ge based on the analysis of measured x-ray-absorption near-edge (XANES) spectra. For a comparison, the results of *c*-Ge are also given.

XANES spectroscopy provides information on the electronic structure of unoccupied states above the Fermi level E_f at a selected atomic site, and a number of solids such as high-T_c superconductors have been studied.[10,11] Results on the electronic structures of melts studied with XANES are still lacking because of the difficulties both in measuring the spectra at high temperature and in analyzing the data for a system for which the atomic configuration is not well defined. We present the measured *K*-edge XANES spectrum of *l*-Ge and a theoretical analysis, to study the electronic pictures of the unoccupied states near E_f by solving the atomic configuration.

The XANES and extended x-ray-absorption fine-structure (EXAFS) measurements using a transmission mode were performed at the beam line BL-10B equipped with a Si(311) channel-cut monochromator at the Photon Factory synchrotron radiation source in Japan. A special sample cell was made of two sapphire tubes with thin closed ends inserted into an open tube in such a way that the closed ends of the inner tubes faced each other with a uniform narrow gap of about 20 μm between them. The closed ends were polished to a thickness of 250 μm in order to improve the efficiency of the x-ray transmission. Special care was taken when filling the gap with Ge melt to keep a uniform thin liquid film vertically in vacuum.[12] In this arrangement, the effect of the sample surface is negligible, and oxidization, as shown in the measurements with the mixtures of sample Ge and inert matrix powders,[6] has not been observed. The similar experiments have been carried out three times, and three measurements have been performed in each experiment.

Figure 1 plots the XANES spectra of *c*-Ge and *l*-Ge taken at room temperature and 1303 K, respectively. The white line of *l*-Ge is more intense, without shoulder features, and is quite smooth on the high-energy side due to disorder, unlike that of *c*-Ge which is full of features. The threshold of the *l*-Ge edge is shifted toward lower energy by about 1.3–1.4 eV related to that of *c*-Ge.

Ab initio one-electron full multiple-scattering[10,13,14] (MS) simulations of the XANES spectra for *c*-Ge and *l*-Ge have been carried out. The real Hedin-Lundqvist self-energy[15] was included as the exchange-correlation potential. The muffin-tin radii were chosen according to the Norman criterion.[16] The calculated spectra were convoluted with a Lorentzian to account for the core-hole lifetime chosen to have a width of 2.35 eV.[17]

The use of x-ray-absorption spectroscopy to determine the unoccupied electronic state band structure near E_f is limited by the final-state effect. Indeed, in the x-ray-absorption process the final states are affected by the core hole, and therefore the ground-state density of unoccupied states could not be probed. According to the final-state rule this effect can be described with the one-electron approximation. In this work,

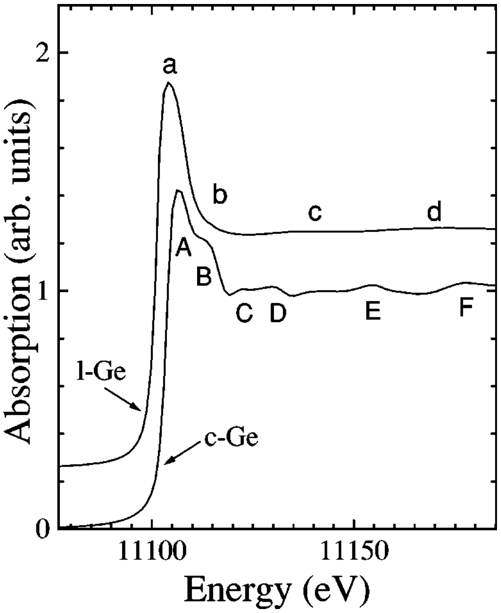

FIG. 1. XANES spectra of *c*-Ge taken at room temperature and of *l*-Ge at 1303 K.

the absorption cross sections were calculated using the MS approach in an unperturbed potential describing the ground-state properties, and in a fully relaxed potential including the core-hole effect by the $Z+1$ approximation[10] to reveal the electronic structure.[18,19]

The calculated XANES spectra in a relaxed and unrelaxed potential for a cluster including 99 atoms of *c*-Ge are presented in Fig. 2(a). Empty spheres are placed in the tetrahedral holes with respect to the diamond lattice. The spectra show a nearly rigid shift of about 3.15 eV toward low energy, and an increase of the white line intensity due to the core-hole-induced relaxation. The agreement with the experimental data is improved by the relaxed potential. All features of the XANES spectrum are well reproduced, indicating that the potential used here is acceptable for germanium in a large enough atomic cluster. The approximation of the optical potential usually is sensitive to the simulation results in the near-edge energy range. The white line (feature *A*) with a shoulder (feature *B*) arises from a projected *p*-like unoccupied density of states (DOS) near E_f, and peaks at higher energy arise from ϵp-like derived bands.

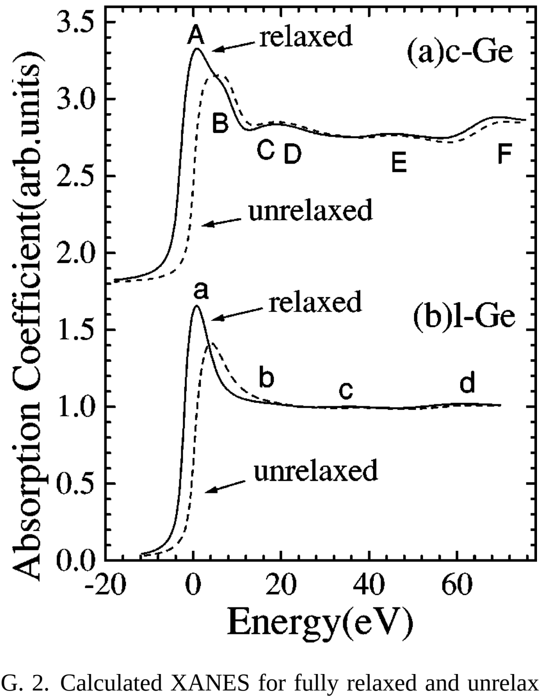

FIG. 2. Calculated XANES for fully relaxed and unrelaxed potentials, for (a) *c*-Ge and (b) *l*-Ge.

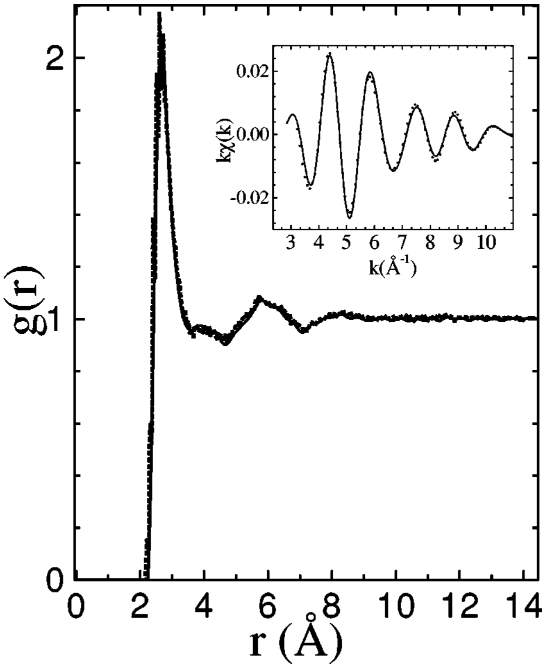

FIG. 3. Pair correlation function of *l*-Ge: solid line, measured data (Ref. 4); dashed line, simulation. Inset: EXAFS: solid line, experimental; dotted line, simulation.

In order to calculate the XANES spectra of *l*-Ge, we have to know its atomic configuration first. A reverse Monte Carlo (RMC) simulation[20] with 1000 atoms based on the EXAFS and neutron-diffraction data[4] has been carried out to create configurational models for *l*-Ge. After 10^5 steps, a series of independent configurations are obtained. The pair-correlation function and the *K*-edge EXAFS of *l*-Ge have been well reproduced from these models, as shown in Fig. 3. The simulations predict a broad, homogeneous distribution of the local bonding configurations, which is in agreement with molecular-dynamics (MD) simulations.[21] Other methods could have been used to obtain the configurations as well, such as MD simulation with a suitable potential which is fit to the experimental conditions. Yet the RMC simulation is simpler here, and is connected with the measurement directly. Sixteen configurations have been randomly taken from the series of the independent converged configurations generated by the RMC simulation, and one cluster located in the center of each configuration has been constructed for XANES simulation. The results of this choice would be similar to that of selecting independent cites in one configuration as cluster centers.[22]

K-edge XANES spectra of *l*-Ge have been calculated with an *ab initio* full MS approach by using atomic clusters constructed according to the independent converged configurations. The calculated spectra averaged over 16 configurations are given in Fig. 2(b). Two cluster sizes have been used for the calculations: a radius of about 3.6 Å covering the main peak in the pair-correlation function, and a radius of about 9 Å covering three coordination shells in the $g(r)$ function. After averaging, the two spectra obtained by using different cluster sizes are almost the same, and compare quite well with the experiment. Hence for disordered systems like *l*-Ge, in contrast with crystals, the general character of the electronic states can be described by the short-range properties with the long-range coordinates as an averaged background in a series of independent configuration models. By averaging the spectra in more configurations, the consistency with experiment should be improved.

The final-state effect on the *K*-edge XANES of *l*-Ge is shown in Fig. 2(b). The white line is shifted by the electron-hole excitonic interaction by 2.75 eV toward lower energy, while peaks *b*, *c*, and *d* in the continuum show only a nearly rigid shift of about 2 eV in the relaxed potential. The excitonic shift of the white line is less than that for *c*-Ge, indicating that the core hole is more screened in *l*-Ge and, therefore, that *l*-Ge is more metallic. On the other hand, the relaxed potential improves the agreement of the calculated XANES of *l*-Ge with the measured data, especially for the white line intensity, indicating the incomplete screening in contrast with normal metals.[11] Hence the molten Ge is not so metallic as normal metals.

In order to check the electronic structure near E_f, DOS calculations were performed by using the self-consistent linear muffin-tin orbital method in the atomic sphere approximation.[23,24] Spare empty spheres were used for the *c*-Ge calculation, and 60-atom supercells from independent atomic configurations which can produce almost the same pair-correlation function as that derived from a large ensemble were used for *l*-Ge DOS calculation.

The *l*-Ge DOS attributed to *s* and *p*-like bands averaging over 16 configurations is presented in Fig. 4 compared with that of *c*-Ge. The energy origin is at the calculated E_f. There is a pseudogap between a predominantly *s*-like lower-energy part and a *p*-like higher-energy part of the band for *l*-Ge. This is consistent with MD calculations[21,25–28] and a photoemission measurement[29] (which can only reflect the electronic states below E_f). The DOS of *l*-Ge remains high around E_f, as in a metal, while that for *c*-Ge ''sees'' a gap there. Above E_f the densities of the empty states both for *l*-Ge and *c*-Ge are quite high, which contributes to the high white lines in the XANES spectra. The peak value of the unoccupied DOS for *l*-Ge is not very much higher than that for *c*-Ge, but the measured white line of *l*-Ge is much higher due to the core-hole relaxation as seen in the XANES calculation, showing that *l*-Ge is not so metallic as a normal metal.

Approximately taking the core-hole effect into account by using the $Z+1$ approximation to simulate the potential of excited atom, the calculated *p*-like DOS in the vicinity of the absorbing atom shown in Fig. 5 indicates that there is a DOS ''piling up'' caused by the core-hole–electron interaction. This enhanced *p*-like DOS is compatible with the high white line of the *l*-Ge *K*-edge XANES. This is consistent with previous XANES calculations.

The *p*-like projected DOS in the conduction band of *c*-Ge contributes to features *A* and *B*, while the *p*-like partial DOS of *l*-Ge only contributes to feature *a*; therefore, the unoccupied *p*-like band for *l*-Ge is much narrower than that for *c*-Ge. This is consistent with the fact that *l*-Ge has long-range disorder.

In summary, based on our measured XANES spectra of molten and crystalline germanium, a MS simulation and a self-consistent DOS calculation have been carried out to study the electronic structures near E_f. In the case of *l*-Ge, the configurations needed for the spectra and DOS calculations were generated by RMC simulation by using the EXAFS and neutron-diffraction data. The calculations repro-

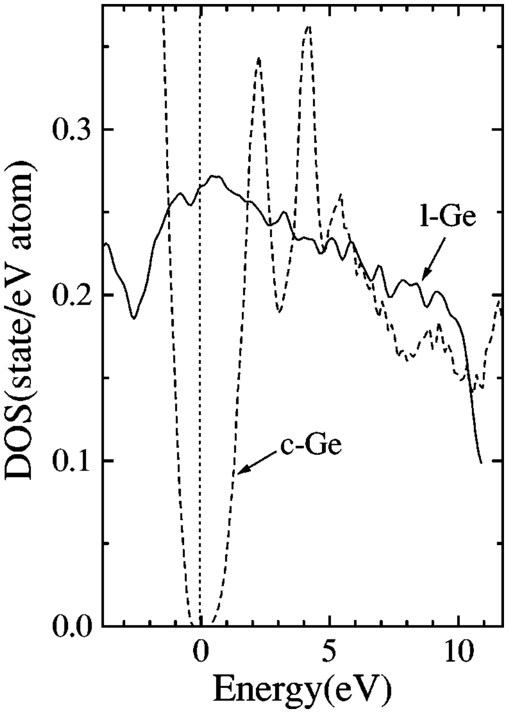

FIG. 4. The *p*-like+*s*-like partial DOS of *c*-Ge (dashed line) and *l*-Ge averaging over 16 configurations (solid line).

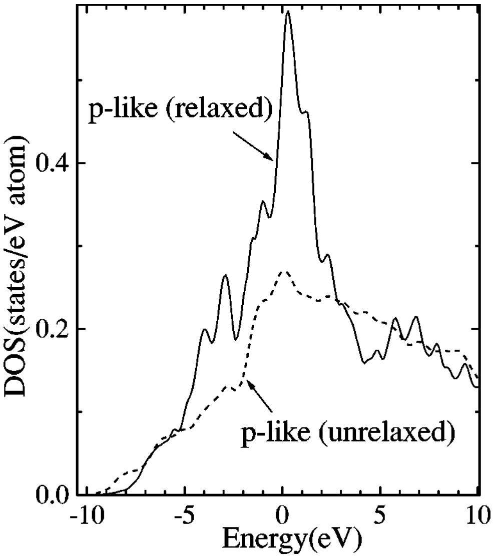

FIG. 5. Calculated *p*-like DOS in the vicinity of the absorbing atom with ground-state (dashed line) and $Z+1$ approximation (solid line) potentials for the absorbing atom.

duce and explain the main features of measured spectra. The strong white line of l-Ge shows a high DOS near E_f, and is partially due to the excitonic effect. l-Ge is not so metallic as normal metals. The DOS of l-Ge is quite high around E_f as for a metal, while that for c-Ge exhibits a gap there. There is a p-like DOS ''piling up'' in the vicinity of the absorbing atom caused by the core-hole–electron interaction. One must take the core-hole effect into account, and then obtain a picture of the ground-state density of unoccupied states measured by XANES, especially in the energy range near E_f.

We are grateful to Dr. P. S. Salmon for sending us his neutron-diffraction data. This research was supported by the Chinese National Natural Science Foundation and a grant for a Key Research Project in the Climbing Program from the State Science and Technology Commission of China.

---

*Present address: Institute of Physical, Nuclear and Macromolecular Chemistry, Philipps University of Marburg, D-35032 Marburg, Germany.

[1] A. F. Ioffe and A. R. Regel, Prog. Semicond. **4**, 238 (1960).

[2] T. E. Enderby and A. C. Barnes, Rep. Prog. Phys. **53**, 85 (1990).

[3] M. P. Tosi, J. Phys.: Condens. Matter **6**, A13 (1994).

[4] P. S. Salmon, J. Phys. F **18**, 2345 (1988).

[5] Y. Waseda, *The Structure of Non-Crystalline Materials* (McGraw-Hill, New York, 1980).

[6] V. Petkov, S. Takeda, Y. Waseda, and K. Sukiyama, J. Non-Cryst. Solids **168**, 97 (1994).

[7] B. R. Orton, in *Neutron and X-ray Scattering*, edited by M. C. Fairbanks, A. N. North, and R. J. Newport, IOP Conf. Proc. No. 101 (Institute of Physics and Physical Society, Bristol, 1990), p. 77.

[8] A. Filipponi and A. Di Cicco, Phys. Rev. B **51**, 12 322 (1995).

[9] A. Filipponi, M. Borowski, P. W. Loeffen, S. De Panfilis, A. Di Cicco, F. Sperandini, M. Minicucci, and M. Giorgetti, J. Phys.: Condens. Matter **10**, 235 (1998).

[10] P. J. Durham, in *X-ray Absorption: Principle, Applications, Techniques of EXAFS, SEXAFS, XANES*, edited by R. Prinz and D. Koningsberger (Wiley, New York, 1988).

[11] A. Bianconi, in *X-ray Absorption: Principle, Applications, Techniques of EXAFS, SEXAFS, XANES* (Ref. 10).

[12] S. Hosokawa, K. Tamura, M. Inui, and H. Endo, J. Non-Cryst. Solids **156-158**, 712 (1993).

[13] C. R. Natoli and M. Benfatto, J. Phys. (Paris) **47**, C8-11 (1986).

[14] J. J. Rehr, J. Mustre de Leon, S. I. Zabinsky, and R. C. Albers, J. Am. Chem. Soc. **113**, 5135 (1991).

[15] H. Chou, J. J. Rehr, E. A. Stern, and E. R. Davidson, Phys. Rev. B **35**, 2604 (1987).

[16] J. G. Norman, Mol. Phys. **81**, 1191 (1974).

[17] K. Rahkonen and K. Krause, At. Data Nucl. Data Tables **14**, 139 (1974).

[18] A. Bianconi, C. Li, S. Della Longa, and M. Pompa, Phys. Rev. B **45**, 4989 (1992).

[19] C. Li, M. Pompa, S. Della Longa, and A. Bianconi, Physica C **178**, 421 (1991).

[20] R. Mcgreevy and L. Pusztai, Mol. Simul. **1**, 359 (1988).

[21] G. Kresse and J. Hafner, Phys. Rev. B **49**, 14 251 (1994).

[22] P. Kizler, Phys. Rev. Lett. **67**, 3555 (1991).

[23] O. K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984).

[24] H. L. Skriver, *The LMTO Method*, Springer Series in Solid-State Sciences, Vol. 41 (Springer, Berlin, 1984).

[25] W. Jank and J. Hafner, Phys. Rev. B **41**, 1497 (1990).

[26] N. Takeuchi and I. Garzon, Phys. Rev. B **50**, 8342 (1994).

[27] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).

[28] R. V. Kulkarni, W. G. Aulbur, and D. Stroud, Phys. Rev. B **55**, 6896 (1997).

[29] G. Indlekofer, P. Oelhafen, R. Lapka, and H. J. Güntherodt, Z. Phys. Chem., Neue Folge **157**, 465 (1988).