PHYSICAL REVIEW B VOLUME 50, NUMBER 2 1 JULY 1994-II

High-pressure studies of solid iodine by Raman spectroscopy

H. Olijnyk
Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

W. Li* and A. Wokaun
Physikalische Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany

(Received 4 January 1994; revised manuscript received 25 March 1994)

Raman spectra of solid iodine were measured up to 26.8 GPa. New bands observed above 10 GPa are discussed within the framework of a previously suggested quasi-one-dimensional molecular phase existing prior to molecular dissociation. Higher-order spectra due to two- and three-phonon processes were observed up to 10 GPa, and provide information on the pressure dependence of phonon states near the edge of the Brillouin zone.

INTRODUCTION

Solid iodine undergoes a molecular to metallic transition around 16 GPa, as evidenced by electrical resistivity[1,2] and optical reflectivity measurements.[3] High-pressure x-ray-diffraction studies provided evidence that the insulator-metal transition was followed by a structural phase transition with molecular dissociation around 21 GPa.[4–6] In disagreement with this conclusion, two high-pressure phases of molecular character, which appear around 16 GPa and around 24 GPa, were proposed on the basis of Mössbauer-effect measurements at 4 K.[7] Subsequent x-ray-diffraction studies at temperatures down to 35 K (Ref. 8) and Mössbauer experiments at 75 K and at room temperature[9] confirmed the respective results. Therefore, a proposed explanation that the discrepancy might be due to a different phase behavior of solid iodine at room temperature and in the low-temperature regime[10] does not appear to be valid. The possibility of an isostructural phase transition before molecular dissociation has also been stressed in a theoretical study.[11]

In previous high-pressure Raman-scattering experiments four out of six first-order Raman-active modes were observed up to 21 GPa.[12,13] The softening of the librational A_g mode and the stretching B_{3g} mode observed upon approaching the dissociation pressure of 21 GPa, as well as the complete disappearance of the Raman spectrum at 24.6 GPa, were taken as strong support for the dissociation concept and the suggested high-pressure structure (D_{2h}^{25}*Immm*, one atom per primitive unit cell).

Second-order Raman spectra were observed in thin iodine films at 80 K for ambient pressure, and were attributed to overtone scattering as well as to combinations of intramolecular phonons with lower frequency lattice modes.[14] In the present study first-order Raman spectra were observed up to 24.6 GPa, and higher-order Raman spectra up to ≈10 GPa.

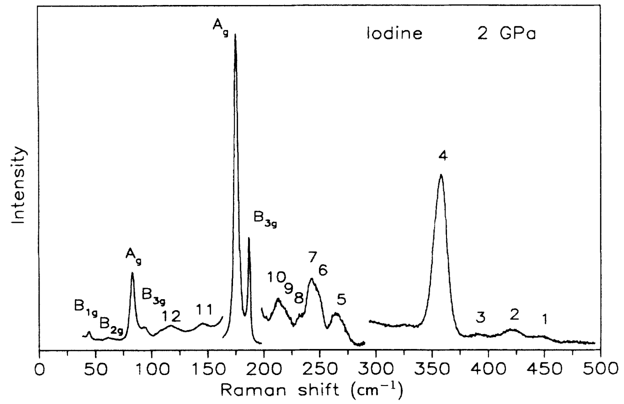

FIG. 1. Raman spectrum of solid iodine at a pressure of 2 GPa. Higher-order bands are labeled by numbers.

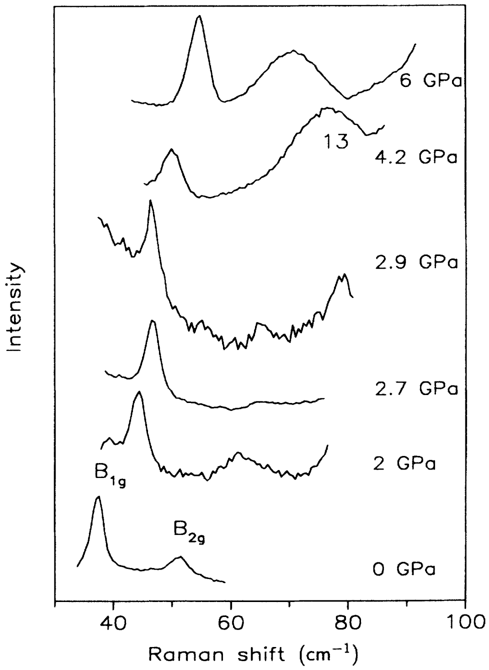

FIG. 2. Raman signals of the librational modes B_{1g} and B_{2g} at various pressures.

©1994 The American Physical Society

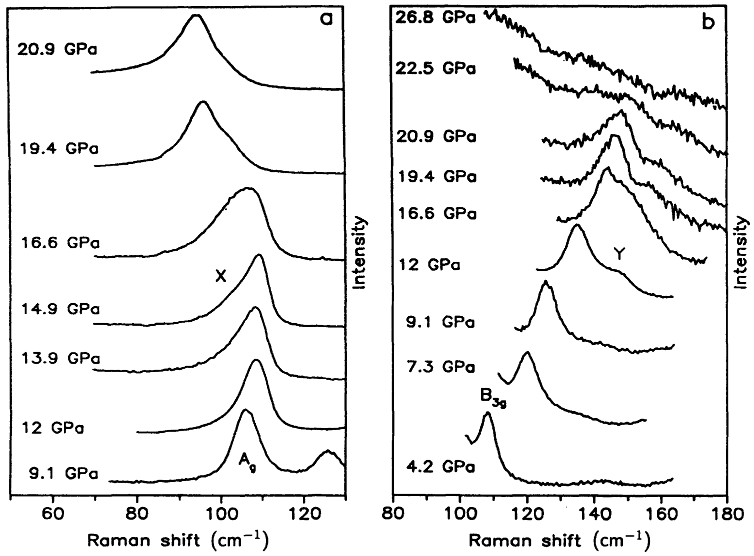

FIG. 3. (a) Raman spectra in the frequency range of the librational A_g mode at various pressures. (b) Raman spectra in the frequency range of the librational B_{3g} mode at various pressures.

EXPERIMENT

The present experiments were performed with a Syassen-Holzapfel diamond-anvil cell.[15] Pressure was determined by the ruby fluorescence method.[16,17] The pressure distribution within the sample chamber was determined by observing the fluorescence from ruby chips at several locations. Pressure inhomogeneities gradually increased with pressure, reaching 2 GPa at the highest pressures applied.

Commercial bisublimated polycrystalline iodine was used as sample material. The 647-nm line of a Kr^+ laser, with a spot size of 20 μm, was used for excitation. Backscattered Raman light was analyzed using a triple spectrograph (Spex, model 1877) equipped with liquid-nitrogen-cooled CCD multichannel detector (Photometrics Ltd.).

RESULTS AND DISCUSSION

The survey Raman spectrum of solid iodine at 2 GPa in Fig. 1 shows all six Raman-active $k=0$ phonon modes, as identified by the corresponding symmetry species. The additional features labeled by numbers are due to higher-

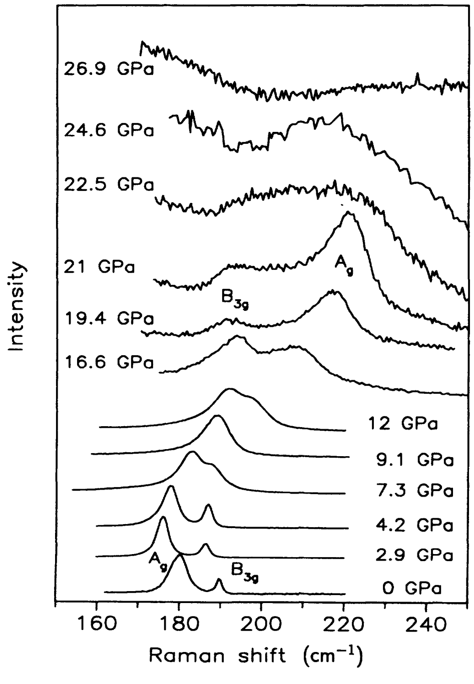

FIG. 4. Raman spectra of the internal modes at various pressures.

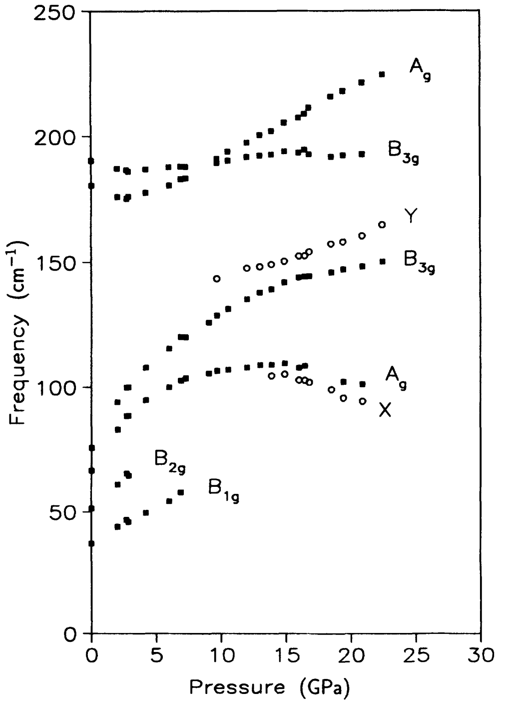

FIG. 5. Pressure-induced shifts of the observed frequencies of first-order Raman bands.

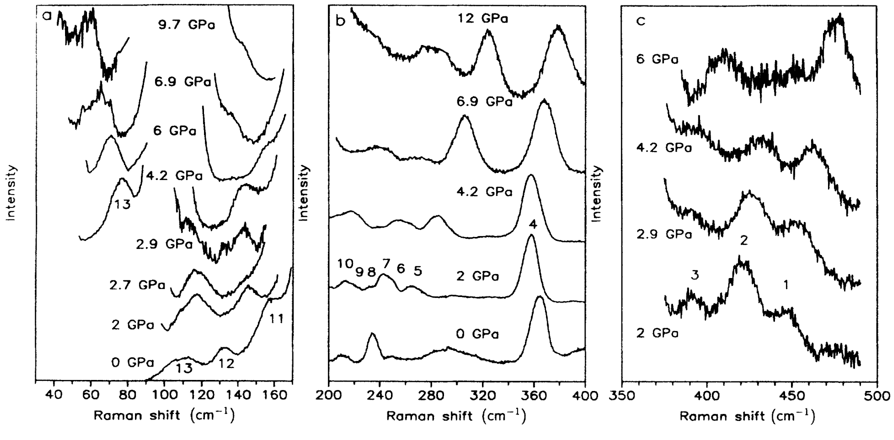

FIG. 6. Higher-order Raman spectra of solid iodine at various pressures.

order processes, to be discussed below.

In comparison to earlier high-pressure Raman studies of first-order Raman spectra,[12,13] the following additional observations have been made in the present investigation. The pressure dependence of the two low-frequency modes B_{1g} and B_{2g} could be followed up to 6 and 2.7 GPa, respectively (Fig. 2). At higher pressures these modes become unobservable due to their small intensities or due to overlap with other bands. The evolution with pressure of the librational A_g mode [Fig. 3(a)] suggests that a new peak (labeled X) emerges on the low-frequency side and grows in intensity, whereas the original peak has nearly vanished around 20 GPa. An additional band (Y) appears on the high-frequency side of the librational B_{3g} band above ≈ 10 GPa [Fig. 3(b)]. In the internal mode region (Fig. 4), a crossing of the A_g and B_{3g} modes occurs at 9.5 GPa. The frequency of the A_g mode continues to increase with pressure, whereas the B_{3g} mode exhibits a shallow maximum around 18 GPa followed by a slight decrease, as observed earlier by Hayashi *et al.*[13] The spectral features at 21 GPa, which cannot be explained by continuation of the two internal modes of the low-pressure phase, suggest the appearance of an additional band between the B_{3g} and A_g modes. Above 21 GPa, no peak can be observed in the frequency range where one would expect the internal B_{3g} mode from the given trend. Instead, a broadband, probably a multicomponent structure, is observed at 22.5 and 24.6 GPa. At higher pressures the intensities become so weak that it is difficult to trace any peak out of the background. The pressure shift of all modes described above is shown in Fig. 5.

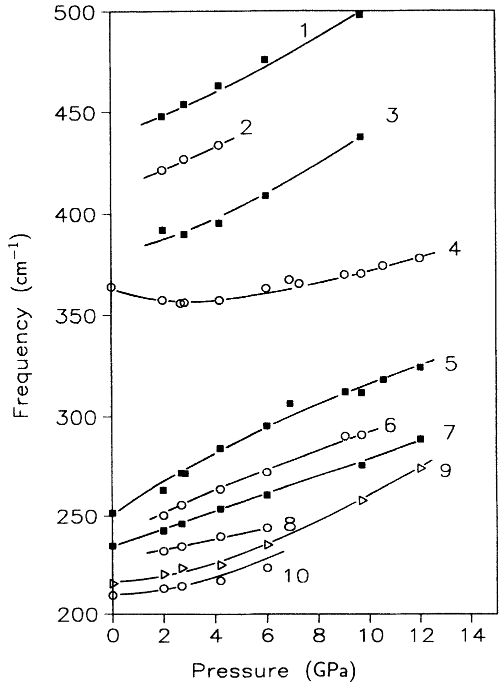

FIG. 7. Pressure-induced shift of higher-order bands observed above 200 cm^{-1}. The solid lines serve as a guide for the eye.

The present observation of the low-frequency lattice modes (B_{1g} and B_{2g}, Fig. 2) in the low-pressure range does not suggest any interpretation different from the model of molecular dissociation.[13] However, from the other observations some questions on the way of molecular dissociation arise. The appearance of two new bands (X, Y) above 10 GPa may be related to the new spectral

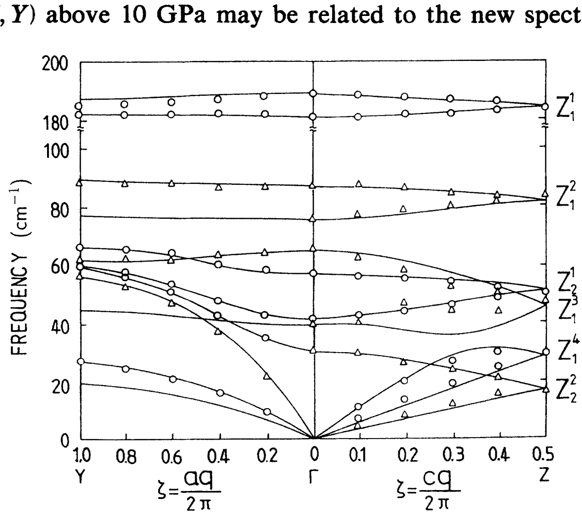

FIG. 8. Dispersion curves of solid iodine along the [100] and [001] directions. Reproduced from Refs. 20 and 21.

components observed in Mössbauer spectroscopy at 16 GPa, which have been explained as the result of the formation of a *quasi*-one-dimensional lattice, i.e., an I_2-I_2 zigzag chain.[7] Conversely, this structure has been regarded as arising from a dimerization of iodine atoms of the high-pressure phase upon decreasing the pressure, as formulated by Takemura *et al.*[6] and by Luthi and Reich.[11]

In the latter study,[11] a quasi-one-dimensional lattice has been predicted on theoretical grounds as a possible phase of solid iodine preceding the molecular dissociation. On the basis of a charge-density-wave concept, molecular dissociation was treated as the reverse process of dimerization or polymerization. It was found that the charge-density distortion caused by the application of pressure increases the charge transfer between neighboring atoms of adjacent molecules in such a way that a *quasi*-one-dimensional lattice can be formed, at pressure below molecular dissociation. Although this intermediate phase was suggested to be of the same symmetry as the normal molecular phase,[11] and would not give rise to any new normal vibrations, the different charge-density distribution of the quasi-one-dimensional lattice would be likely to shift the frequencies of the phonon modes. The new Raman bands observed in our measurements may be regarded as a manifestation of the coupling between phonon modes and charge-density wave. The structure suggested for the high-pressure phase after molecular dissociation has one atom per primitive unit cell,[5] and should not give rise to any Raman spectra. The distinct Raman spectra in the internal mode region observed above 21 GPa might thus be due to a coexistence of low- and high-pressure phases. On the other hand, the observation of a new band in the internal mode region above 19.4 GPa may be also understood within the framework of an intermediate high-pressure phase of molecular character.

Higher-order Raman spectra have been observed in the frequency range up to 500 cm^{-1}, and are shown in Fig. 6. For the bands above 200 cm^{-1} the pressure dependence of the frequencies is displayed in Fig. 7. Above 7 GPa, the distinction of frequencies 6, 7, 8, 9, and 10 becomes difficult as the bands merge. From consideration of the symmetry species of the normal modes, and of the Raman tensor at the symmetry points,[18,19] we find that all overtones and combination bands should be Raman active, except for a few combinations at the center of the Brillouin zone.

By comparing the dispersion curves available from Refs. 20 and 21 (Fig. 8) with the present experimental results, the following assignments can be made. Band 4 is attributed to the overtone spectrum of the internal modes. The features between 200 and 320 cm^{-1} (bands 5–10) are due to two-phonon combinations of the internal modes and lower-frequency lattice modes. The peaks above 400 cm^{-1} (1–3) arise from three-phonon states due to combinations of internal overtones with lattice mode states.

On the basis of this assignment, the frequencies of the involved lattice modes may be determined as a function of pressure, by simply subtracting the known frequencies of the internal overtone states from bands 1–3, and of the first-order internal states (estimated as half the frequencies of the overtone states) from the positions of bands 5–10. Results are shown in Fig. 9(a); we note that the frequencies derived from features 1, 2, and 3 agree with those derived from features 5, 7, and 10, respectively.

Next we turn to the discussion of the three weak bands 11, 12, and 13 observed in the low-frequency region of the spectrum, i.e., below 160 cm^{-1}. It is suggested that these higher-order bands arise from difference transitions between internal phonon states and the lattice mode states. Figure 9(b) compares the experimentally observed pressure shift of the mentioned bands, with possible differences calculated from the internal mode frequencies, and from the lattice modes derived above as shown in Fig. 9(a). The agreement of frequencies 11, 12, and 13 with some of these combinations suggests that these features are in fact due to difference transitions involving

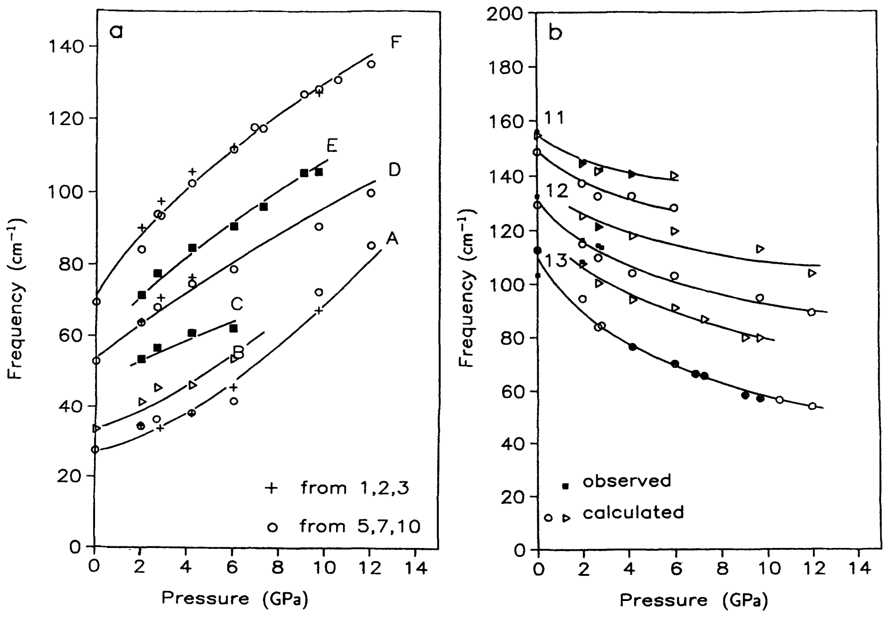

FIG. 9. (a) Pressure-induced shift of the lattice mode states involved in the higher-order Raman bands. Differences between experimentally observed frequencies were calculated as described in the text. The solid lines serve as a guide for the eye. (b) Comparison of observed higher-order bands below 160 cm^{-1}, with possible differences between the frequencies of internal modes and lattice modes, as derived in (a). The solid lines serve as a guide for the eye.

internal phonons and lattice modes.

Proper assignment of the lattice mode states involved in the observed higher-order spectra is rather difficult due to the limited knowledge of the dispersion curves, which have been measured only for the [001] and [100] directions.[20] Moreover, no information is available on the critical points, which are intimately connected with any structure occurring in the higher-order spectra. Based on a comparison of the frequencies of the lattice modes at or near ambient pressure [from Fig. 9(a)] with the available dispersion curves,[20,21] and accounting for a slight temperature shift, the following tentative assignments may be proposed. Modes *A*, *B*, and *F* may be identified with states at or near Z_1^4, Z_1^3, and Z_1^2, respectively (cf. Fig. 8); modes *C*, *D*, and *E* may be attributed to states at or near Z_1^3 and Z_2^1, and near Y around 65 cm^{-1}. Information about critical points can be obtained by analysis of the phonon density of states. Any structure occurring in the higher-order spectra reflects structure in the frequency dependence of the phonon density of states. In our assignment of the higher-order spectra, mainly the Z point was used to account for the observed frequency differences. This may indicate that the Z point is a critical point.

Next we address the relation between zone edge and zone center modes. Comparing Fig. 5 with Fig. 7 we find that the observed frequency of the overtone (band 4 in Fig. 7), which is probably due to states near Z_1^1, shifts with pressure in a manner analogous to the one of the A_g internal mode at lower pressures. At higher pressures, however, the pressure dependence of the overtone is more similar to the one of the B_{3g} internal mode at higher pressure. The frequency shift with pressure of branch Z_1^2 is similar to that of the B_{3g} lattice mode.

Such pressure-induced changes may be related to alterations in the k dependence of the dispersion curves, which in turn may be due to changes of structural parameters and lattice dynamics of iodine under pressure. Theoretical studies[22,23] of the pressure dependence of normal mode frequencies at the Γ point are found to be in qualitative agreement with the experimental results. It is desirable that the present observation will stimulate further theoretical investigations, to gain a better understanding of the lattice dynamics, and of the way of molecular dissociation in solid iodine under pressure.

CONCLUSIONS

The present high-pressure study of solid iodine by Raman spectroscopy reveals the appearance of new bands above 10 GPa. The new features are discussed with respect to a previously suggested *quasi*-one-dimensional molecular phase existing at intermediate pressures before molecular dissociation, and may point out a more subtle way of dissociation than previously proposed on the basis of X-ray-diffraction studies. Higher-order spectra have been observed for the first time up to ≈10 GPa, and are assigned to two- and three-phonon processes involving combinations of lattice mode states near the edge of the Brillouin zone with internal modes and their overtones.

ACKNOWLEDGMENTS

Financial support of this work by grants of the Deutsche Forschungsgemeinschaft (SFB 213) and by the Verband der Chemischen Industrie is gratefully acknowledged.

---

*On leave from the Institute for Laser & Spectroscopy, Zhongshan University, P.R. China.

[1] B. M. Riggleman and H. G. Drickamer, J. Chem. Phys. **37**, 446 (1962); **38**, 2721 (1963).

[2] N. Sakai, K. Takemura, and K. Tsujii, J. Phys. Soc. Jpn. **51**, 1811 (1982).

[3] K. Sysassen, K. Takemura, H. Tups, and A. Otto, in *Physics of Solids Under High Pressure,* edited by J. S. Schilling and R. N. Shelton (North-Holland, Amsterdam, 1981), p. 125.

[4] O. Shimomura, K. Takemura, Y. Fujii, S. Minomura, M. Mori, Y. Noda, and Y. Yamada, Phys. Rev. B **18**, 715 (1978).

[5] K. Takemura, S. Minomura, O. Shimomura, and Y. Fujii, Phys. Rev. Lett. **45**, 1881 (1980).

[6] K. Takemura, S. Minomura, O. Shimomura, Y. Fujii, and J. D. Axe, Phys. Rev. B **26**, 998 (1982).

[7] M. Pasternak, N. J. Farrell, and R. D. Taylor, Phys. Rev. Lett. **58**, 575 (1987).

[8] H. Fujihisa, Y. Fujii, K. Hase, Y. Ohishi, N. Hamaya, K. Tsuji, K. Takemura, O. Shimomura, H. Takahashi, and T. Nakajima, High Pressure Res. **4**, 330 (1990).

[9] M. Pasternak, J. N. Farell, and R. D. Taylor, Phys. Rev. Lett. **59**, 945 (1987).

[10] K. Takemura, O. Shimomura, and Y. Fujii, Phys. Rev. Lett. **59**, 944 (1987).

[11] T. Luthy and J. C. Raich, Can. J. Chem. **66**, 812 (1988).

[12] O. Shimomura, K. Takemura, and K. Aoki, in *High Pressure in Research and Industry,* edited by C. M. Backman, T. Johanisson, and L. Tegner (Uppsala, Arkitektkopia, 1982), p. 272.

[13] Y. Hayashi, Y. Fujii, H. Fujihisa, K. Aoki, H. Yamawaki, O. Shimomura, and K. Takemura, in *Recent Trends in High Pressure Research,* Proceedings of the XIIIth AIRAPT International Conference on High-Pressure Science and Technology, Bangalore, India, 1992 (Oxford IBH, New Delhi, 1992), p. 119.

[14] B. V. Shanabrook and J. S. Lannin, Solid State Commun. **38**, 49 (1981).

[15] W. B. Holzapfel, in *High Pressure Chemistry,* edited by H. Kelm (Reidel, Boston, 1978), p. 177.

[16] R. A. Forman, G. J. Piermarini, J. D. Barnett, and S. Block, Science **176**, 284 (1972).

[17] G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, J. Appl. Phys. **46**, 2774 (1975).

[18] V. Wagner, Phys. Status Solidi B **50**, 585 (1972).

[19] P. J. Grout, J. W. Leech, and P. S. English, J. Phys. C **8**, 1620 (1975).

[20] H. G. Smith, M. Nielsen, and C. P. Clark, Chem. Phys. Lett. **33**, 75 (1975).

[21] K. Toukan and S. H. Chen, Mol. Phys. **44**, 693 (1981).

[22] K. Kobashi and R. Etters, J. Chem. Phys. **79**, 3018 (1983).

[23] P. G. Johannsen, Ph.D. thesis, Paderborn, 1984.