PHYSICAL REVIEW B VOLUME 61, NUMBER 3 15 JANUARY 2000-I

Local structure of bulk amorphous and crystalline $(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$

A. V. Sapelkin and S. C. Bayliss
Solid State Research Center, Department of Chemistry and Physics, De Montfort University, The Gateway, Leicester LE1 9BH, United Kingdom

A. G. Lyapin and V. V. Brazhkin
Institute for High Pressure Physics, Russian Academy of Sciences Troitsk, Moscow Region 142092, Russia

(Received 29 June 1999)

The local structure of bulk amorphous and crystalline $(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ produced by solid-state amorphization and subsequent crystallization of amorphous samples, respectively, have been studied using extended x-ray absorption fine structure. Measurements have been made at the Ga and Ge K edges for $c-(\mathrm{GaSb})_{1-x}\mathrm{Ge}_x$, and at all K absorption edges for $\mathrm{a}-(\mathrm{GaSb})_{1-x}\mathrm{Ge}_x$. All samples are found to be fourfold coordinated with a local structure close to the $c-\mathrm{GaSb}$ or the $c-\mathrm{Ge}$ phase. The partial distances $R_{\text{Ga-Sb}}$, $R_{\text{Ge-Sb}}$, $R_{\text{Ge-Ga}}$, $R_{\text{Ga-Ge}}$, $R_{\text{Sb-Ga}}$, and $R_{\text{Sb-Ge}}$ are shown to be independent of Ge concentration and defined by covalent radii of the components in both materials. The nature of local ordering in the amorphous materials is such that Ge seems to substitute mainly for Sb at lower Ge concentration ($x<30-40$ at. %), aiding relief of stress inserted during amorphization of the material. Crystalline $(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ seems to contain a phase with around 4 Ga/Ge neighbors around Ge along with Ge randomly substituting on Ga and Sb sites in a solid solution. Debye-Waller broadening of amorphous and crystalline $a-(\mathrm{GaSb})_{1-x}\mathrm{Ge}_x$ are of the same order of magnitude, suggesting chemical disorder in the crystalline material.

I. INTRODUCTION

Over the past 15 years there has been a steady stream of papers concerning the structural properties of $(A^{III}B^{V})_{1-x}(C_2^{IV})_x$ alloys.[1–9] These alloys have been synthesized in the form of thin films. A special feature of these alloys is a zinc-blende-to-diamond structural phase transition at some composition in between the pure III-V and group-IV elements. One can distinguish two directions in which discussion has progressed over the years: (i) allowing the existence of chemical disorder in the material (i.e., Ga-Ga and Sb-Sb bonds, see Refs. 1,3,4, and 6), (ii) considering the materials to be chemically ordered (see Refs. 5 and 7). Both groups, however, admitted the existence of the zinc-blende-to-diamond phase transition, which was demonstrated directly by high-resolution x-ray diffraction measurements[4] and differ only on the nature of this transition. It is the issue of local ordering that makes possible the coexistence of these two approaches. Also, most of the above studies are concerned with crystalline alloys, though there are a few studies of amorphous thin films. These latter generally describe the amorphous nature of the films and look at kinetics of crystallization.[3] Despite the importance of the issue of local ordering there were just a few studies of these materials using short range sensitive techniques, such as extended x-ray absorption fine structure (EXAFS) (see, for example, Refs. 2,10, and 11). All these works showed that the nearest-neighbor (NN) bond length is constant (within experimental error) in the materials across the studied concentration range. The alloys were found to be random on the atomic scale, with the exception of Ref. 2, where Ge seemed to concentrate on the grain boundaries in $c-(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$. As to the NN distances, they were found to be conserved and correspond to those in the respective binary materials. We would like to note that the authors of Ref. 11 concluded that the NN distances are changing in $\mathrm{GaAs}_x\mathrm{P}_{1-x}$ versus x, though close inspection of Table II in Ref. 11 leads to the conclusion that the distances are the same within error. We take this subject further here by investigating the local structure of $(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ amorphous and crystalline solid solutions.

The macroscopic properties of disordered tetrahedral semiconductors prepared by solid-state amorphization (SSA) under high pressures[12,13] have been extensively studied.[14–18] These properties however, are defined by the microscopic nature of the materials, and an understanding of this can provide deeper insight into the structure of materials prepared by SSA. Recently, papers have been published on the local structure and long-range structural correlations in SSA $a-\mathrm{GaSb}$ and its solid solutions with Ge.[16,19,20] At the same time it is well-known that no structural technique at present can uniquely describe the structure of an amorphous solid. This is because of the loss of the periodicity in disordered materials and, as a consequence, the relation between structure and symmetry. Therefore, the structure of such substances can only be described in terms of mean values (of, e.g., distances, nearest neighbor numbers, Debye-Waller factors) or, at best, distributions. Thus, the structural description of an amorphous solid is a challenging task even in the case of monoatomic substances. The situation becomes even more complicated for binary or polyatomic materials. The ability of EXAFS to yield significant structural information for binary amorphous materials has been recently demonstrated for a range of sputtered amorphous films[21–23] and for bulk amorphous GaSb prepared by SSA.[19]

Although the possible influence of Ge on macroscopic and structural properties was discussed previously,[15,16] to our knowledge there is only one paper (Ref. 14) that describes the local structure of $a-(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$. In that paper, $a-(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ studied using x-ray diffraction showed anomalies in the behavior of coordination numbers and shell distances determined up to $x\approx 0.29$. It was found that the

0163-1829/2000/61(3)/1907(5)/$15.00

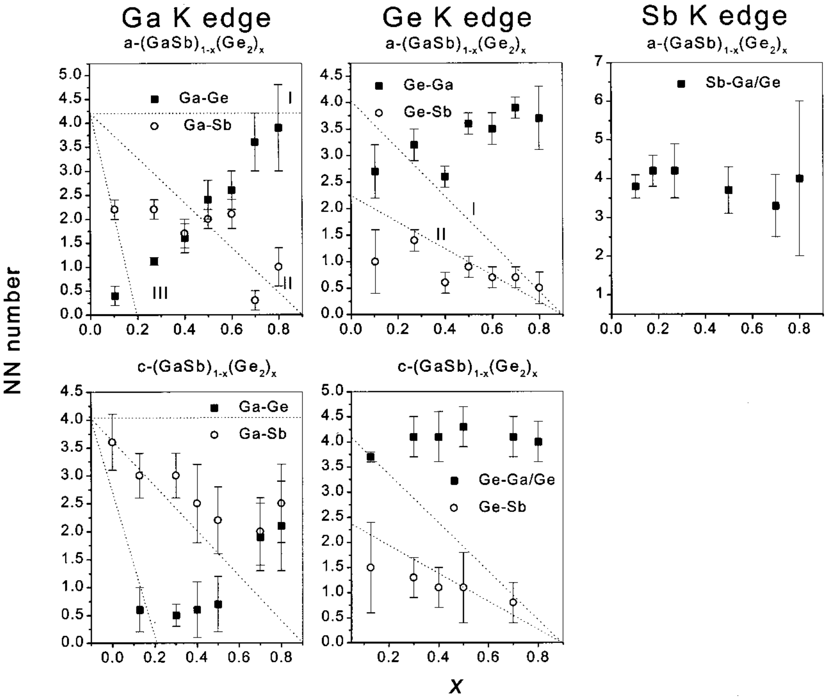

FIG. 1. The concentration dependence of nearest-neighbors coordination numbers around Ga (a) and Ge (b) centers in $(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$. Ga *K* edge (a): solid squares—$N_{\text{Ga-Sb}}$, open squares— $N_{\text{Ga-Ge}}$. Ge *K* edge (b): solid squares—$N_{\text{Ge-Sb}}$, open squares—$N_{\text{Ge-Ga}}$. Sb *K* edge (c): solid squares— $N_{\text{Sb-Ge(Ga)}}$, open squares—$N_{\text{Sb-Ga}}$. Sb *K* edge was fitted assuming either Ga or Ge neighbors. I—Ge substitutes for Ga only; II—equally for Ga and Sb; III—for Sb only. Fig. 1, bottom row: I—Ge substitutes for Ga only; II—equal substitution; III—for Sb only (this line coincides with zero ordinate).

radius of the first coordination sphere increases with increase of Ge content, in contrast to what would be expected for GaSb doped with Ge since the covalent radius of Ge (1.22 Å) is smaller than the covalent radii of Ga (1.26 Å) and Sb (1.32 Å). This increase in bond length and also the change in ratio N_2/N_1 from 2.7 to 3 were ascribed to a transition from a highly strained amorphous network (with some crystalline impurities of Ge and GaSb) into the homogeneous amorphous solid solution. However, from the point of view of our recent investigations of the local structure of $a-$GaSb using EXAFS,[19] the conclusion about anomalous increase of bond length with introduction of Ge seems less well founded.

In this paper we present the results of an investigation of local structure of these materials by EXAFS at all *K*-absorption edges (Ga, Ge, Sb). Using the advantages of EXAFS for studies of local structure we have been able to extract partial (not averaged as in the case of Ref. 14) structural parameters ($R_{\text{Ga-Sb}}$, $R_{\text{Ge-Sb}}$, $R_{\text{Ga-Ge}}$, $R_{\text{Sb-Ga, Ge}}$, etc.).

II. EXPERIMENT

Amorphous $(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ was prepared by the high pressure SSA technique described earlier.[12,24] Note that samples of $a-$GaSb normally contain up to 1-3% of $c-$GaSb.[12,13] The experimental procedure of collection and analysis of EXAFS spectra are described in details elsewhere (see Ref. 19 and references therein). Experiments were carried out at ambient conditions on stations 7.1 (Ga and Ge *K* edges) and 9.2 (Ga, Ge, and Sb *K* edges) at CLRC Daresbury Laboratory synchrotron radiation source. Samples of $c-(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ were obtained from the corresponding amorphous ones by annealing as described in Ref. 25. After preparation all samples were checked by x-ray diffraction.

III. EXPERIMENTAL RESULTS

The concentration dependencies of the numbers of nearest neighbors extracted from EXAFS data are presented in Fig. 1. Broken lines (I, II, and III) represent three ideal modes of substitution of Ge into GaSb. Fig. 1, top row: I—Ge substitutes for Ga only; II—equally for Ga and Sb; III—for Sb only. Fig. 1, bottom row: I—Ge substitutes for Ga only; II—equal substitution; III—for Sb only (this line coincides with zero ordinate). The Sb *K*-edge first-shell coordination numbers were fitted assuming either Ge or Ga neighbors. This procedure is valid due to the essentially similar scattering power of Ge and Ga atoms and therefore their equivalence from the point of view of EXAFS. This can be seen in Fig. 1—both fitting procedures give the same result. For the same reason Ge and Ga *K*-edge coordination numbers of neighbors other than Sb were obtained assuming either Ga and Ge neighbors, respectively (i.e., no Ga-Ga and Ge-Ge bonds).

EXAFS results allow us to suggest that there is observable change in the dependence of N_{Sb} versus x at both Ge and Ga edges. One can see from the Ga *K* edge that data points do not follow any particular mode of substitution. Rather they spread in the area which corresponds to preferable substitution of Ge for Sb (especially in the region of lower concentration x). The same situation is also true for Ge *K* edge data. In the latter case, however, one can observe the tendency for equal substitution at high-Ge concentrations more clearly. A similar behavior of the number of nearest neighbors versus Ge concentration was observed in $c-(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ studied by EXAFS.[2] In that paper, the effect was ascribed to Ge preferably substituting for Sb at the grain boundaries, thus relaxing possible stresses. One can also see that the total number of nearest neighbors in the material at all concentrations of Ge stays close to four (Fig. 1, top row). The next figure (Fig. 2) presents the concentration dependencies of nearest neighbor distances at all edges studied. Here, we can see that all the distances are essentially independent of concentration of Ge. Note that neutron scattering experiments[20] also indicate that the bond length in $a-$GaSb does not noticeably change from that of $c-$GaSb. The results of this paper and the ones published recently on EXAFS (Ref. 19) and neutron diffraction[20] suggest that there

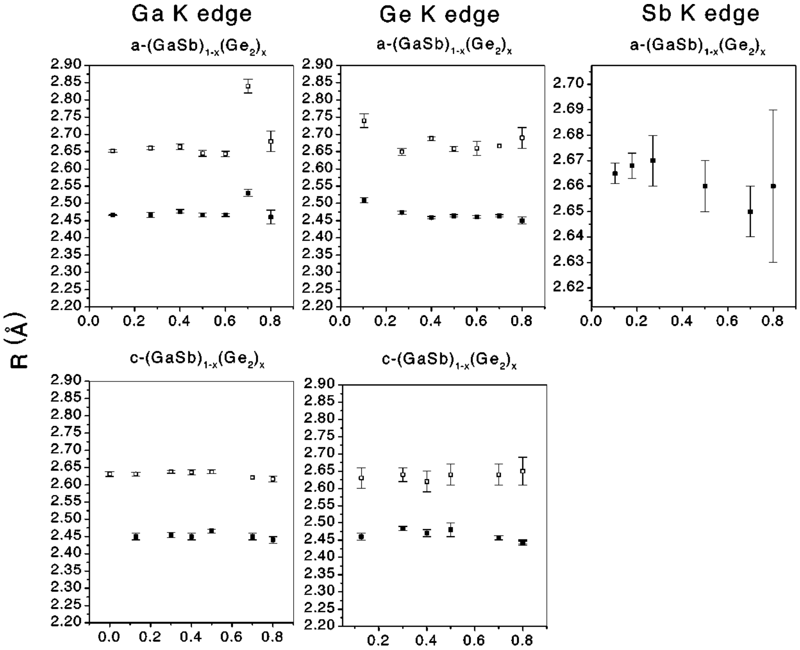

FIG. 2. The nearest-neighbor distances around Ga (a) and Ge (b) centers in $(GaSb)_{1-x}(Ge_2)_x$ versus concentration of Ge x. Ga K edge (a): solid squares—$R_{\text{Ga-Sb}}$, open squares— $R_{\text{Ga-Ge}}$. Ge K edge (b): solid squares—$R_{\text{Ge-Sb}}$, open squares—$R_{\text{Ge-Ga}}$. Sb K edge (c): solid squares— $R_{\text{Sb-Ge}}$(Ga), open squares—$R_{\text{Sb-Ga}}$.

exist instead significant distortions of bond angles in $a-(GaSb)_{1-x}(Ge_2)_x$ rather than in nearest-neighbor distances.

Our EXAFS results are also confirmed by neutron diffraction from samples of $a-$(GaSb) and $a-(GaSb)_{0.73}(Ge_2)_{0.27}$ (see total correlation function, Ref. 26). We found that first and second-shell distances are higher for $a-$GaSb [$R_1=2.65(2)$ Å and $R_2=4.32(5)$ Å] than those for $a-(GaSb)_{0.73}(Ge_2)_{0.27}$ [$R_1=2.61(2)$ Å and $R_2=4.23(5)$ Å] indicating no significant changes in average bond length as found in Refs. 14 and 10. We can also determine the value of the bond angle ϕ for $a-(GaSb)_{0.73}(Ge_2)_{0.27}$ from the first and second peak positions in the total correlation function (see Ref. 26) giving $\phi_a-(GaSb)_{0.73}(Ge_2)_{0.27}=108(1)°$, while ϕ_a-GaSb$=110(1)°$ and ϕ_c-GaSb$=109.47°$. Thus all the angles are close to the ideal tetrahedral value found in $c-$GaSb.

We also investigated $c-(GaSb)_{1-x}(Ge_2)_x$ obtained from amorphous samples by the technique described in Ref. 25. The corresponding results for NN numbers and NN distances are presented in the bottom rows of Figs. 1 and 2. We found some distinctive differences in Ge substitution compared to that for $a-(GaSb)_{1-x}(Ge_2)_x$. One can see that the NN number behavior corresponds to the model of equal substitution much better than in the corresponding amorphous solutions. The other feature is that the number of Ge/Ga atoms around Ge is around 4 and constant throughout the concentration range. Figure 3 shows the EXAFS Debye-Waller broadening for amorphous and crystalline samples. One can

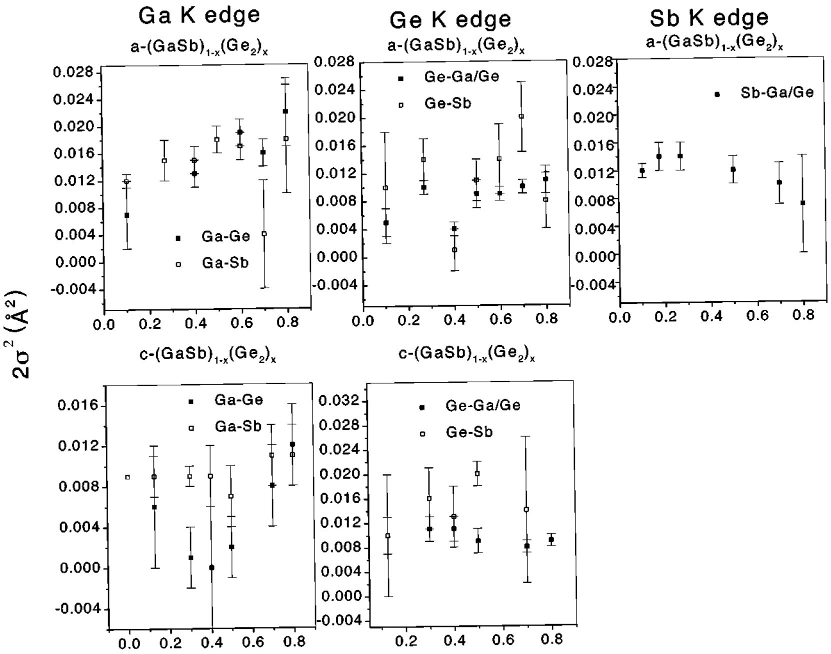

FIG. 3. The concentration dependence of nearest-neighbor Debye-Waller factors around Ga (a) and Ge (b) centers in $(GaSb)_{1-x}(Ge_2)_x$. Ga K edge (a): solid squares—$N_{\text{Ga-Sb}}$, open squares— $N_{\text{Ga-Ge}}$. Ge K edge (b): solid squares—$N_{\text{Ge-Sb}}$, open squares—$N_{\text{Ge-Ga}}$. Sb K edge (c): solid squares— $N_{\text{Sb-Ge(Ga)}}$, open squares—$N_{\text{Sb-Ga}}$.

see that the values of Debye-Waller (DW) broadening are comparable for both sets of samples.

IV. DISCUSSION

Our EXAFS results show that total coordination in $a-(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ is close to 4 throughout the concentration range. The NN distances are also constant and one can conclude that bond length is determined by the covalent radii of compounds and not affected by introduction of Ge. These results suggest the short range structure of the material is close to those of $c-\mathrm{GaSb}$ (Zn-blende structure) or $c-\mathrm{Ge}$ (diamond structure). The only exception is the point at $x=0.7$ and this is due to strong correlation of distances with DW factors for the corresponding spectrum. In fact, it is possible to bring the values in line with the rest of the data points by fixing the appropriate DW factors (see Fig. 3). We, however, preferred to follow the general data analysis procedure for all data sets by minimizing the parameters, which characterize the goodness of fit in EXCURV92.

The role of Ge in $a-\mathrm{GaSb}$ can be understood if we recall that III-V semiconductors in general and GaSb in particular are understood to be slightly ionic in character. This means that in the case of GaSb negative charge transfers from Ga to Sb. This charge transfer could make Ga-Sb-Ga and Sb-Ga-Sb angles in general different, as can be observed in the low-temperature EXAFS measurements[19] at Sb and Ga *K* edges. While nearest-neighbor-Debye-Waller (DW) factors are the same at both edges [0.0044(4) Å^2], the second-neighbor DW factors are not [0.012(1) Å^2 at Ga *K* edge and 0.009(1) Å^2 at Sb *K* edge]. The stress inserted on $a-\mathrm{GaSb}$ during amorphization would make the bond angles even more different. This difference could well be responsible for Ge substituting for Sb at lower x because such substitution would lower the ionicity of a bond, thus increasing the stability of the structure. This would explain EXAFS results presented in this paper. It would also explain the observed increase of pressure of the structural phase transition in $a-(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ with increase of Ge concentration (see, for example, Ref. 16). Thus, we can suggest that introduction of Ge leads to the relaxation of stresses related to angle distortions in $a-\mathrm{GaSb}$. This would not significantly affect the nearest neighbor distances, and we can see from EXAFS that it does not. Annealing of amorphous samples to obtain $c-(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ is then thought to result in relief of stresses and redistribution of Ge.

The behavior of Ge in $c-(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ indicates that it not only randomly substitutes for Ga and Sb. In fact, it seems that there is a tendency for phase separation and presence of Ga/Ge rich areas throughout the concentration range. This follows from Fig. 1 since the total coordination of Ge with Ga/Ge neighbors is around 4, and at the same time the Sb concentration corresponds to random substitution of Ge for Ga and Sb.

In general, Ge seems to act as a stress relief agent in GaSb, lowering the total energy of the solution compared to that of $a-\mathrm{GaSb}$, mainly substituting for Sb in the areas of maximum stress at lower concentration. This follows from the analysis of the distribution of numbers of nearest neighbors (Fig. 1). At higher concentrations the distribution tends to follow the case of the homogeneous solution. The $a-(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ seems to have a structure close to that of $c-\mathrm{GaSb}$ I phase (tetrahedral), with the number of nearest neighbors in the first coordination shell close to four.

The exact microscopic description of the mechanism of Ge incorporation in GaSb is still to be established. Also a model needs to be built of $a-(\mathrm{GaSb})_{1-x}(\mathrm{Ge}_2)_x$ in terms of atomic positions, and the information collected to date on the local structural properties of these solutions could be extremely valuable in this respect. A theoretical model that would explain preference of angle over bond-length distortions has still to be built.

ACKNOWLEDGMENTS

We gratefully acknowledge DMU and CCLRC Daresbury Laboratory for financial support through CASE (for A.V.S.), CCLRC Daresbury Laboratory for beam-time and computer facilities, and the Royal Society for the FSU-UK joint project grant. A.G.L. and V.V.B. also thank the Russian Foundation for Basic Research for financial support (Grant No. 98-02-16325). We would like to thank Dr. F. Mosselmans for help with EXAFS experiments on station 9.2 at CCLRC Daresbury Laboratory.

---

[1] K.E. Newman, A. Lastras-Martinez, B. Kramer, S.A. Barnett, M.A. Ray, J.D. Dow, and J.E. Greene, Phys. Rev. Lett. **50**, 1466 (1983).

[2] E.A. Stern, F. Ellis, K. Kim, L. Romano, S.I. Shah, and J.E. Greene, Phys. Rev. Lett. **54**, 905 (1985).

[3] K.C. Cadien, B.C. Muddle, and J.E. Greene, J. Appl. Phys. **55**, 1482 (1984).

[4] S.I. Shah, B. Kramer, S.A. Barnett, and J.E. Greene, J. Appl. Phys. **59**, 1482 (1986).

[5] H. Holloway and L.C. Davis, Phys. Rev. Lett. **53**, 830 (1984).

[6] B.-L. Gu, K.E. Newman, and P.A. Fedders, Phys. Rev. B **35**, 9135 (1987).

[7] L.C. Davis and H. Holloway, Phys. Rev. B **35**, 2767 (1987).

[8] A. Lastras-Martinez, G. Rodriguez-Pedroza, D.H. Mei, B. Kramer, D. Lubben, and J.E. Greene, Phys. Rev. B **43**, 14 035 (1991).

[9] R. Osório and S. Froyen, Phys. Rev. B **47**, 1889 (1993).

[10] J.C. Mikkelsen, Jr. and J.B. Boyce, Phys. Rev. B **28**, 7130 (1983).

[11] Z. Wu, K. Lu, Y. Wang, J. Dong, H. Li, C. Li, and Z. Fang, Phys. Rev. B **48**, 8694 (1993).

[12] S.V. Demishev, Y.V. Kosichkin, A.G. Lyapin, N.E. Sluchanko, M.M. Aleksandrova, V.I. Larchev, S.V. Popova, and G.G. Skrotskaya, J. Non-Cryst. Solids **97&98**, 1459 (1987).

[13] V.V. Brazhkin, A.G. Lyapin, S.V. Popova, and R.N. Voloshin, Zh. Éksp. Teor. Fiz. **56**, 156 (1992) [JETP Lett. **56**, 152 (1992)].

[14] V.V. Brazhkin, A.G. Lyapin, S.V. Popova, S.V. Demishev, Y.V. Kosichkin, D.A. Lunts, N.E. Sluchanko, and S.V. Frolov, Zh. Éksp. Teor, Fiz. **104**, 3126 (1993) [Sov. Phys. JETP **77**, 465 (1993)].

[15] V.A. Sidorov, V.V. Brazhkin, L.G. Khvostantsev, A.G. Lyapin,

A.V. Sapelkin, and O.B. Tsiok, Phys. Rev. Lett. **73**, 3262 (1994).

[16] V.V. Brazhkin, A.G. Lyapin, L.G. Khvostantsev, V.A. Sidorov, O.B. Tsiok, S.C. Bayliss, A.V. Sapelkin, and S.M. Clark, Phys. Rev. B **54**, 1808 (1996).

[17] A.G. Lyapin, V.V. Brazhkin, S.V. Popova, and A.V. Sapelkin, Phys. Status Solidi B **198**, 481 (1996).

[18] V.V. Brazhkin, A.G. Lyapin, V.A. Goncharova, O.V. Stalgorova, and S.V. Popova, Phys. Rev. B **56**, 990 (1997).

[19] A.V. Sapelkin, S.C. Bayliss, A.G. Lyapin, V.V. Brazhkin, and A.J. Dent, Phys. Rev. B **56**, 11 531 (1997).

[20] O.I. Barkalov, A.I. Kolesnikov, V.E. Antonov, E.G. Ponyatovski, U. Dahlborg, M. Dahlborg, and A. Hannon, Phys. Status Solidi B **198**, 491 (1996).

[21] N. Elgun, S.J. Gurman, and E.A. Davis, J. Phys.: Condens. Matter **4**, 7759 (1992).

[22] S.H. Baker, S.C. Bayliss, S.J. Gurman, N. Elgun, J.S. Bates, and E.A. Davis, J. Phys.: Condens. Matter **5**, 519 (1993).

[23] S.H. Baker, S.C. Bayliss, S.J. Gurman, N. Elgun, and E.A. Davis, J. Phys.: Condens. Matter **8**, 1591 (1996).

[24] S.V. Demishev, Y.V. Kosichkin, D.A. Lunts, A.G. Lyapin, N.E. Sluchanko, and M.S. Sharambeyan, Zh. Éksp. Teor. Fiz. **100**, 707 (1991) [Sov. Phys. JETP **73**, 394 (1991)].

[25] V.V. Brazhkin, A.G. Lyapin, S.V. Popova, and N.V. Kalyaeva, J. Mater. Sci. **30**, 443 (1995).

[26] A.V. Sapelkin, S.C. Bayliss, A.G. Lyapin, V.V. Brazhkin, and A.J. Dent, J. Synchrotron Radiat. **6**, 492 (1999).