Semiconductor-metal and superconducting transitions induced by pressure in amorphous As_2Te_3 †

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The resistivity and activation energy ΔE in $\rho = \rho_0 \exp(\Delta E/kT)$ of flash evaporated amorphous As_2Te_3 films were found to decrease gradually with increasing pressure until $\rho \sim 8 \times 10^{-4}$ Ω cm becomes temperature independent near 100 kbar. This gradual transition contrasts with the abrupt transitions occurring at 60 kbar in a-Ge and 100 kbar in a-Si. The metallic amorphous As_2Te_3 becomes superconducting at 4.4 ± 0.1 K and 100 kbar. The resistivity nearly returns to its original value after release of pressure at 300 K. The opposite sign of the pressure coefficients of the optical parameters in tetrahedral and chalcogenide materials suggests that a gradual spreading of the bands and closing of the gap occurs in chalcogenide glasses. In tetrahedral materials a sudden increase in coordination seems to take place at a critical pressure.

I. INTRODUCTION

Amorphous semiconductors have attracted considerable interest and have been studied extensively because their electronic and optical properties are quite different from those of crystalline semiconductors. In particular, the pressure-induced semiconductor-metal transition is an interesting phenomenon. Amorphous Si and Ge were found to show a pressure-induced semiconductor-metal transition.[1-3] Their transition pressures (100 kbar for a-Si, 60 kbar for a-Ge) are lower by a factor of about 0.6 than those in crystalline Si and Ge,[4] where the pressure induces a structural change from a diamond-type structure with four coordinations to a β-Sn type structure with six coordinations.[5] High-pressure metallic phases of amorphous semiconductors remain amorphous.

A few chalcogenide glasses have also been investigated at high pressures. Among these were sputtered $Ge_{16}As_{35}Te_{28}S_{21}$ which transforms gradually into the metallic state near 150 kbar, and evaporated As_2S_3 and As_2Se_3.[6] These last two materials are still semiconducting at 250 kbar, the highest pressure reached. By extrapolating the pressure dependence of the resistivity to higher pressures one expects metallic conduction near 450 kbar for As_2S_3 and near 300 kbar for As_2Se_3.

Recently, Mott proposed a double-injection model for the on-state in a chalcogenide threshold switch.[7] In this model the semiconductor-metal transition is thought to be induced by an electric field. Mott pointed out that the electron-hole gas may also be responsible for the metallic conduction in the pressure-induced metallic state of amorphous semiconductors.

The present paper reports about the pressure-induced semiconductor-metal transition and super-conducting transition in flash evaporated amorphous As_2Te_3. This material was chosen because the results obtained by Minomura et al. suggest that the critical pressure scales roughly with the energy gap of the semiconductor. The small activation energy makes it likely that the metallic state is reached at pressures below 110 kbar, the limit of our apparatus. Moreover, As_2Te_3 belongs to a group of amorphous lone-pair semiconductors, which are distinguished from tetrahedrally bonded amorphous semiconductors.[8]

II. EXPERIMENTAL

The high-pressure apparatus for the measurements of the electrical resistance of amorphous As_2Te_3 as a function of pressure and temperature consists of a hydraulic press and supported taper cell for cryogenic temperatures. The hydraulic press for cryogenic temperatures is similar to that which was discussed by Shimomura et al.[1] except for the structure of the tension member as shown in Fig. 1. The compression member, the cylindrical tension member, and the table are made of austenitic stainless steel (AISI type 321). The supported taper cell is constructed with opposed tapered pistons of sintered tungsten carbide with 5% cobalt binder and a cylinder of sintered tungsten carbide with 13% cobalt binder.

The cylinder has four holes for a four-lead system. The electrical resistance cell developed by Balchan and Drickamer[9] was modified to permit the introduction of more than four leads. The supported taper cell and the sample assembly are shown in Fig. 2. This cell has a leakage resistance of about 10^9 Ω.

The supported taper cell was loaded by the hydraulic press at room temperature. After precooling with liquid nitrogen it was then cooled to
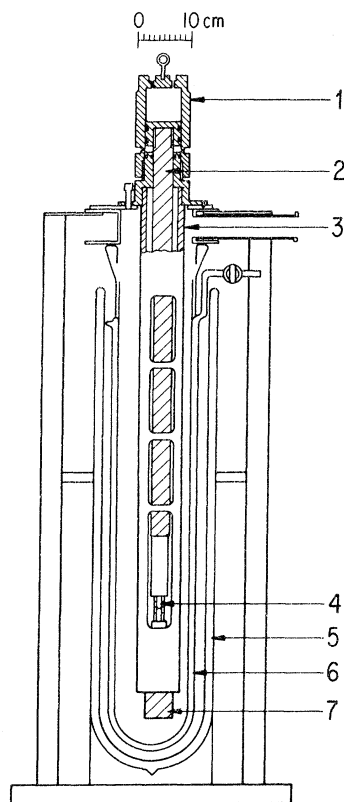
FIG. 1. Hydraulic press for cryogenic temperatures (1) press head, (2) compression member, (3) tension member, (4) supported taper cell, (5) nitrogen Dewar, (6) helium Dewar, (7) threaded plug connecting (2) and (3).

liquid-helium temperatures. The pressures were calibrated at 300 K using as fixed points the Bi transitions at 25.5 and 77 kbar and the Sn transition at 97 kbar. The pressures at cryogenic temperatures were regarded as the same as those calibrated at room temperature. This is permissible because the design of the apparatus is such that the differential thermal contraction between the compression and tension members is negligible. The temperature was measured by a copper-constantan thermocouple and by a carbon resistor attached to the outside of the supported taper cell cylinder.

Amorphous films of As_2Te_3 were prepared on a mica substrate maintained at room temperature by flash evaporation. The starting vacuum was 2×10^{-7} Torr. The aluminum electrodes of a thickness of about 4000 Å with separations of 0.1 mm were evaported on the ~20-μm-thick mica substrate and then the amorphous As_2Te_3 of a thickness of about 6500 Å and a width of 0.2 mm was deposited to bridge the separation. The film thickness during the deposition was monitored by a Sloan

quartz crystal. The deposition rate was 40 Å/sec. The mica with the sample on it was cut into small pieces ($1 \times 1 \times 0.02$ mm) for the measurement of electrical resistance at high pressures. The x-ray diffraction pattern of the film deposited on glass at the same time as the sample was being deposited on the mica did not show any crystalline peaks.

III. RESULTS

Figure 3 shows the change in resistivity as a function of pressure for amorphous As_2Te_3 at room temperature. Our samples show a resistivity of the order of 10^4 Ω cm at zero pressure. With an increase of pressure, the resistivity decreases continuously and becomes of the order of 10^{-4} Ω cm at 100 kbar. The change of resistivity with decreasing pressure shown in Fig. 3 was recorded by means of the same pressure scale as that used in the compression process. The resistivity after decreasing pressure to about 1 bar was of the order of 10^3 Ω cm. This resistivity was smaller by one order of magnitude than that of the initial material.

The relatively large hysteresis between the resistivity curves measured with increasing and decreasing pressure, respectively, is a common artifact in such high-pressure measurements. The pressure in the sample cell can only be calibrated with fair accuracy by means of Bi and Sn samples for increasing pressure. As the pressure is released in the press head (1) of Fig. 1, the pressure around the sample remains clamped and decreases only slowly because of the densification and de-
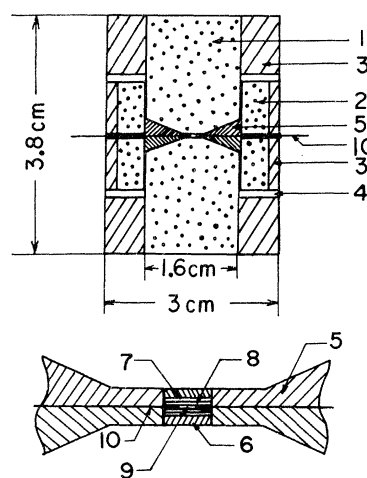

FIG. 2. Supported taper cell and sample assembly (1) sintered tungsten carbide piston, (2) sintered tungsten carbide cylinder, (3) stainless-steel jacket, (4) Teflon, (5) pyrophyllite pellet, (6) pyrophyllite disk, (7) AgCl film, (8) upper mica, (9) sample evaporated on mica, (10) copper wire.
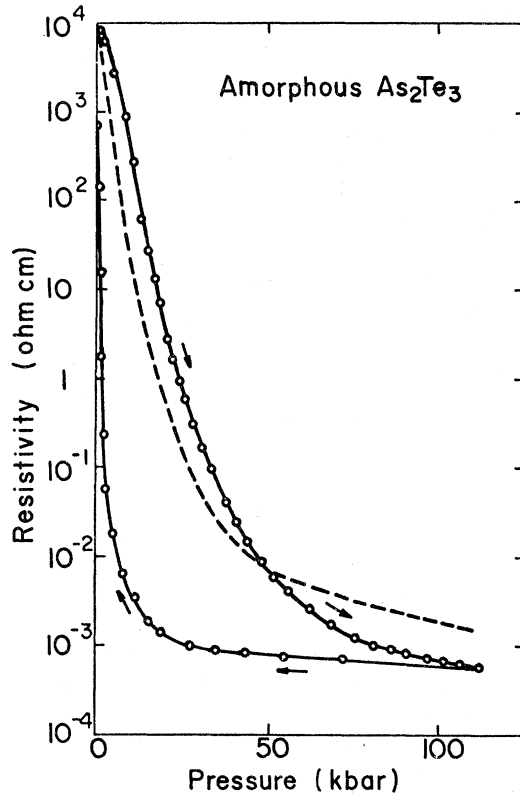
FIG. 3. Resistivity vs pressure for amorphous As_2Te_3 at room temperature. Note the gradual decrease in resistivity with increasing pressure. The dashed curve is calculated from $\rho = \rho_0 \exp(\Delta E/kT)$ assuming $\rho_0 = $ const. and ΔE varying with P as shown in Fig. 4.

formation of the pyrophyllite pellet enclosing the sample. This residual pressure is also partly responsible for the fact that the sample resistivity does not return to its original value. The calibration points of the Bi and Sn samples show a similar hysteresis upon release of pressure. For the analysis of the data we have used only the resistivity curve measured at increasing pressures.

The temperature dependence of the resistivity under high pressures is of the form of $\rho = \rho_0 \times \exp(\Delta E/kT)$ over the temperature range investigated from 300 to 77 K. The slope ΔE from $\log_{10}\rho$ vs $1/T$ is plotted as a function of pressure in Fig. 4. ΔE decreases continuously to zero near 100 kbar with increasing pressure. Because of the limited temperature range studied it is not clear whether the small temperature dependence of the resistivity above $P = 50$ kbar is to be attributed to an activation energy ΔE or whether it is due to hopping conduction in a high density of localized states near the Fermi level. Nevertheless, amorphous As_2Te_3 transforms continuously into the metallic state completing its transformation at about 100 kbar. This semiconductor-metal transi-

tion is reversible.

At this point an operational definition of metallic conduction is called for. We consider the conductivity metallic if its temperature coefficient is zero or negative and if its value is equal or larger than Mott's[10] minimum metallic conductivity, 10^3–10^4 Ω^{-1}cm^{-1}. Above 100 kbar the conductivity of amorphous As_2Te_3 is larger than 10^3 Ω^{-1}cm^{-1} and temperature independent down to $T = 4.4$ K, the onset of superconductivity. We have not yet investigated whether the conductivity between say 60 and 100 kbar becomes temperature independent below 77 K and perhaps superconducting at low temperatures. Because of the continuous nature of the transition, its critical pressure remains somewhat uncertain.

The broken curve in Fig. 3 represents the calculated ρ-P curve, $\rho = \rho_0 \exp(\Delta E/kT)$, where the experimental result of Fig. 4 was used for the pressure dependence of ΔE, and the preexponential factor ρ_0 (~2×10^{-3} Ω cm at 1 bar) was assumed to be independent of the pressure. This assumption was made because a small hysteresis of the resistance with decreasing and increasing temperature at high pressure made an accurate determination of ρ_0 at high P impossible. In the present experiment the thermocouple was attached at a distance of about 1.5 cm from the sample. Therefore there might have been a temperature difference in spite of the slow cooling rate (~1 K/min). However, ΔE with increasing temperature. The fairly good agreement between the experimental and calculated curves indicates that the pressure effect on the activation energy constitutes the main contribution
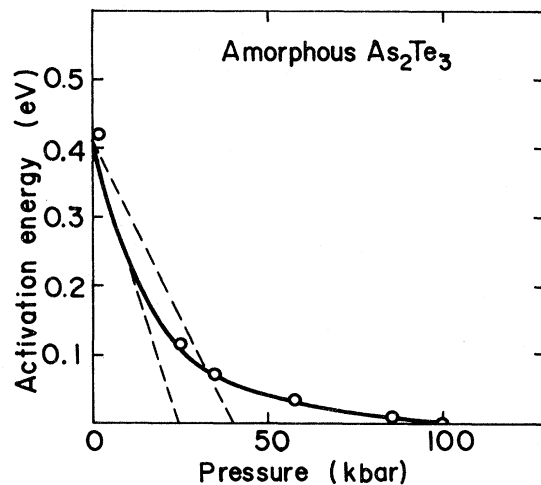

FIG. 4. Activation energy ΔE from $\rho = \rho_0 \exp(\Delta E/kT)$ as a function of pressure. The dashed lines represent the range of decrease of ΔE expected from the pressure coefficient of the optical gap of several chalcogenide glasses.
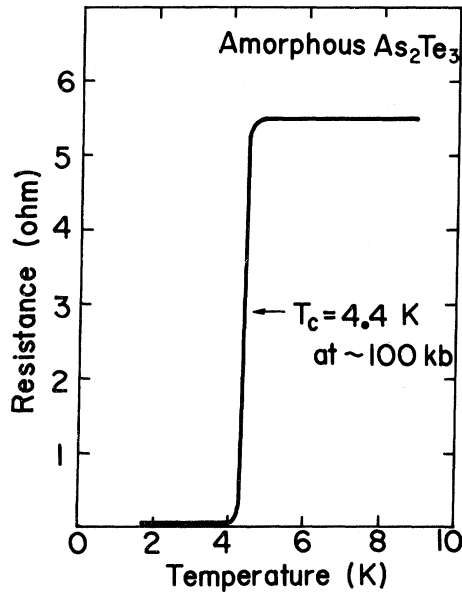
FIG. 5. Superconducting transition of the pressure-induced metallic amorphous As_2Te_3.

to the pressure dependence of the resistivity of amorphous As_2Te_3.

Figure 5 shows the superconducting transition of the pressure-induced metal in amorphous As_2Te_3. The superconducting transition temperature T_c was 4.4 ± 0.1 K at about 100 kbar when measured at the point of a sharp rise in resistance during slow increase of temperature. It is clear that the superconductivity is not due to the presence of filamentary As or Te. These elements show superconducting transitions at high pressure in the crystalline state, but their transition temperatures, $T_c = 0.2$ K at 100 kbar for As,[11] and $T_c = 3.3$ K at 56 kbar for Te,[12] are much lower than the T_c of amorphous As_2Te_3.

IV. DISCUSSION

The behavior of the pressure-induced semiconductor-metal transition in tetrahedral materials is very different from that in chalcogenide glasses. As shown in Fig. 6, the resistivity of tetrahedral semiconductors[1-3,13] decreases abruptly by many orders of magnitude at a critical pressure. The striking difference between the two material classes manifests itself already at lower pressures.

The effect of pressure on the electrical and optical properties of crystalline group IV and III-V tetrahedral semiconductors has been reviewed by Paul and Warschauer.[14] In Ge the indirect optical gap first increases, as Γ-L transitions dominate; it then reaches a maximum and decreases with pressure as the minimum gap is determined by Γ-X transitions. The direct gaps of GaAs and InSb

increases and the indirect Γ-X gap of Si slightly decreases with pressure. Important is that in all tetrahedral materials the gap is rather large up to the critical pressure of the semiconductor-metal transition. This is qualitatively verified by recent measurement of Welber[15] and Welber et al.[16,17] The last authors[17] found for instance that the gap of Si is reduced by only 20% near $P = 120$ kbar, where a first-order transformation to the metallic phase occurs. This is the same transition which Minomura et al.[2] observe at $P = 150$ kbar, see Fig. 6. In amorphous tetrahedral materials including amorphous Si, the optical gap increases and the refractive index decreases with pressure.[18,19] The pressure dependence of the resistivity is more complicated because it is not only determined by the gap but also by the mobility and the position of the Fermi level.[14] Moreover, the inhomogeneous distribution of the pressure in the Drickamer cell causes experimental difficulties: the high resistance of the material in the central high-pressure region is short circuited by the lower resistance of surrounding material which is still at lower pressure. We noticed this effect when we observed the superconducting transition at $T_c = 4.4$ K in amorphous As_2Te_3 at $P = 100$ kbar. For $T < T_c$ the resistance is still finite because some small portions of the sample in series with the supercon-
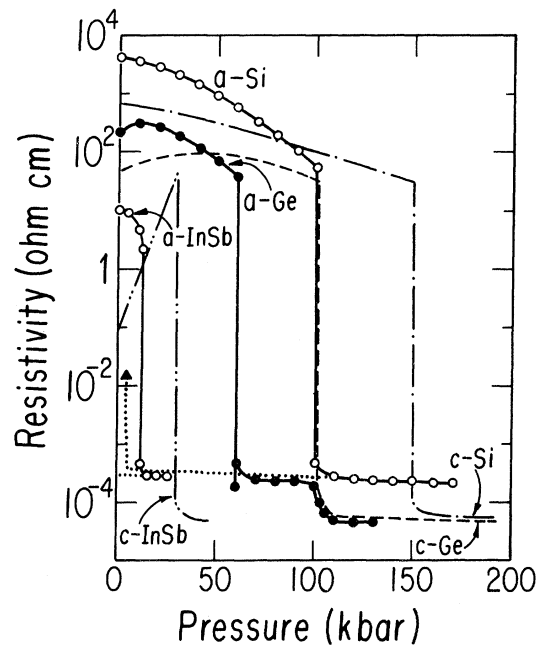

FIG. 6. Resistivity vs pressure for amorphous and crystalline Si, Ge, and InSb at room temperature. The full curves refer to amorphous material and the dashed-dotted lines to the corresponding crystals. Note that the transitions occur abruptly at a critical pressure. (Reproduced with kind permission of Minomura et al., Ref. 2.)

ducting phase are still normal. In addition, the detailed pressure behavior of the resistivity of amorphous tetrahedral semiconductors depends on preparation conditions.[20] Nevertheless, the resistivity data are in accord with the persistance of a finite gap to the critical pressure.

The optical gap of chalcogenide glasses, on the other hand, decreases with pressure at a rate between -1×10^{-5} and -2×10^{-5} eV/bar.[19] These rates, measured at low pressures, are shown by the dashed lines in Fig. 4. As far as we know the optical gap of chalcogenide glasses has not yet been studied at high pressures but it is likely that it continues to decrease. This would be in agreement with our electrical measurements shown in Fig. 4 because the thermal activation energy ΔE of the resistivity and the optical gap E_0 of most chalcogenide semiconductors are related approximately as $\Delta E \approx \frac{1}{2} E_0$, which means that the Fermi level is near the center of the gap. We therefore seem to observe a gradual decrease of the gap with pressure. This decrease of the gap is accompanied by an increase in the dielectric constant which further tends to decrease the localization of gap states and promotes metallic conduction at high pressures.

The situation is different in[6,21] Se and[12] Te which show a sudden jump to metallic conduction at $P_c \approx 100-130$ kbar and $P_c \approx 40$ kbar, respectively, but only after the resistivity has decreased by many orders of magnitude. The metallic phases become superconducting near $T_c = 7$ K and $T_c = 3.3$ K, respectively. McCann and Cartz[22] observed that amorphous Se slowly crystallizes under pressure and eventually develops near 140 kbar the same as yet undetermined high-pressure structure as hexagonal Se. Pressure measurements of the elastic constants of trigonal Se and Te show[23] a continuous decrease of the anisotropy and suggest that the high-pressure form is nearly sixfold coordinated and thus metallic. The gradual closing of the gap in Se and Te seems to be terminated by a sudden phase transformation.

This does not seem to occur in amorphous As_2Te_3. According to Cornet and Rossier,[24] the structure of amorphous As_2Te_3 is different from that of crystalline As_2Te_3 even as far as the short-range order is concerned. The monoclinic As_2Te_3 consists of complex zigzag chains in which the arsenic atoms are octahedrally and trigonally bonded to tellurium atoms, whereas all tellurium atoms are threefold coordinated.[25] The octahedrally bonded sites, that is those with sixfold coordination, do not exist in the amorphous state. These high coordination sites yield the quasimetallic character of the crystalline compound. One might argue that the high coordination of the monoclinic As_2Te_3 appears again in the amorphous metallic phase of As_2Te_3 at high pressures. We believe this is unlikely because crystalline As_2Te_3 undergoes a high-pressure phase transition.[26] This phase transition was detected by the method of differential thermal analysis at high pressures. The phase boundary between the two modifications was represented by the expression $P(\text{kbar}) = 8.5 + \frac{1}{6} [455 - t(°C)]$ in the region up to 18 kbar. One can expect a phase transition at about 80 kbar and room temperature by extrapolation of this relation. If so, it would be interesting to compare the pressure-induced metallic character of amorphous As_2Te_3 with the high-pressure modification of crystalline As_2Te_3.

Although only a few materials have been studied, it is tempting to conclude that the pressure-induced semiconductor-metal transition in chalcogenide glasses is quite different from that in tetrahedral materials. In tetrahedral materials, a decrease of the lattice spacing with increasing pressure strengthens the covalent bond and thus increases the gap.[19] The sudden transition to the metallic phase at a critical pressure appears to be due to a sudden increase in coordination. In chalcogenide glasses on the other hand the pressure does not alter the covalent bonds as much as it increases the overlap of the lone-pair states and thus the width of the bands.[19] The gradual spreading of the bands closes the gap and produces the metallic state when the density of states at the Fermi level becomes sufficiently large.

[1]O. Shimomura, S. Minomura, N. Sakai, K. Asaumi, K. Tamura, J. Fukushima, and H. Endo, Philos. Mag. 29, 547 (1974).
[2]S. Minomura, O. Shimomura, N. Sakai, K. Asaumi, H. Endo, K. Tamura, J. Fukushima, and K. Tsuji, AIP Conf. Proc. 20, 234 (1974).
[3]K. Tamura, J. Fukushima, H. Endo, S. Minomura, O. Shimomura, and K. Asaumi, J. Phys. Soc. Jpn. 36, 558 (1974).
[4]S. Minomura and H. G. Drickamer, J. Phys. Chem. Solids 23, 451 (1962).

[5]J. C. Jamieson, Science 139, 762 (1963).

[6]S. Minomura, K. Aoki, O. Shimomura, and K. Tanaka, Sixth International Conference on Amorphous and Liquid Semiconductors, Leningrad, USSR (1975) (unpublished).

[7]N. F. Mott, Philos. Mag. 32, 159 (1975).

[8]M. Kastner, Phys. Rev. Lett. 28, 355 (1972).

[9]H. S. Balchan and H. G. Drickamer, Rev. Sci. Instrum. 32, 308 (1961).

[10]N. F. Mott, Philos. Mag. 22, 7 (1970).

[11]I. V. Berman and N. B. Brandt, JETP Lett. 10, 55 (1969).

[12]B. T. Matthias and J. L. Olsen, Phys. Lett. 13, 202 (1964).

[13]O. Shimomura, K. Asaumi, N. Sakai, and S. Minomura (unpublished).

[14]W. Paul and D. M. Warschauer, in *Solids under Pressure* (McGraw-Hill, New York, 1963), p. 179.

[15]B. Welber, Rev. Sci. Instrum. 47, 183 (1976).

[16]B. Welber, M. Cardona, C. K. Kim, and S. Rodriguez (unpublished).

[17]B. Welber, C. K. Kim, M. Cardona, and S. Rodriguez (unpublished).

[18]G. A. N. Connell and W. Paul, J. Non-Cryst. Solids 8-10, 215 (1972).

[19]M. Kastner, Phys. Rev. B 6, 2273 (1972); 7, 5239 (1973).

[20]D. L. Camphausen, G. A. N. Connell, and W. Paul, J. Non-Cryst. Solids 8-10, 223 (1972).

[21]J. Wittig, Phys. Rev. Lett. 15, 159 (1965).

[22]D. R. McCann and L. Cartz, J. Chem. Phys. 56, 2552 (1972).

[23]R. M. Martin, T. A. Fjeldly, and W. Richter, Solid State Commun. 18, 865 (1976).

[24]J. Cornet and D. Rossier, J. Non-Cryst. Solids 12, 85 (1973).

[25]G. J. Carron, Acta Crystallogr. 16, 338 (1963).

[26]V. G. Yakushev and V. A. Kirkinskii, Dokl. Akad. Nauk SSSR 186, 882 (1969).