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METALLIC PROPERTIES OF ORTHORHOMBIC HIGH PRESSURE PHASE OF GaAs: THEORY & EXPERIMENT

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Contrary to current beliefs that GaAs II is a semiconductor or semimetal, we find that the two high pressure orthorhombic phases of GaAs (GaAs II and GaAs III) are metallic and superconducting with T_c close to 4.5 K. Results from the experimental measurements and first principles pseudopotential calculations are found to be consistent.

Introduction

Because of their central role as prototype solids, the properties of high pressure phases of the elemental covalent semiconductors, Si and Ge, have been studied extensively.[1,2] One salient feature of these high pressure phases is that they are metallic and superconducting.[3-5] In Si the superconducting transition temperature T_c has the rather high value of 8.7 K,[4] considering that Si is not a transition metal and does not contain any d-electrons. Studies of such systems have contributed to our understanding of structural phase transitions and the details of the mechanisms of phonon-mediated superconductivity.

Although the corresponding III-V compound semiconductors with the zincblende structure, such as GaAs, have also been known to undergo several pressure induced solid-solid phase transitions,[1,6-8] relatively little is known about the properties of their high pressure phases. For example it has been suggested that GaAs transforms into an orthorhombic phase near 17 GPa.[6,7] The structure of this high pressure phase has not been uniquely identifed until recently. Using x-ray diffraction with synchrotron radiation, Weir *et al.*[9] have identified two different orthorhombic phases, instead of one, and a "simple hexagonal" (SH) phase for GaAs (labelled as GaAs II, GaAs III and GaAs IV by these authors). GaAs II is stable between 17 and 24 GPa while GaAs III is stable between 24 and 60 GPa. Above 60 GPa, GaAs IV, which is similar to the SH phase of GaSb,[10,11] is stable. The crystal structures for the GaAs II and GaAs III phases have also been suggested by Weir *et al.*[9] based on their experiment. Enlightened by these results, the atomic positions, the equilibrium lattice parameters and the internal parameter α of GaAs II have been obtained recently by *ab initio* pseudopotential calculations.[12]

Theoretical calculations suggest that the high pressure phases of GaAs are metallic[8] but the only electrical resistance experiment performed so far has concluded that at least one of the high pressure orthorhombic phases (GaAs II) is semiconducting or semimetallic but not metallic.[1] If this conclusion were correct, then GaAs behaves differently than Si and Ge. Furthermore, the experimental result would disagree with results of pseudopotential calculations which have found that all the high pressure structures of GaAs tested, *i.e.*, NaCl, NiAs and β-Sn structures, are metallic.[8] Thus it is desirable to investigate the electronic properties of the high pressure orthorhombic phases of GaAs. In this paper we present an experimental and theoretical study of GaAs under high pressure using a diamond anvil cell and *ab initio* pseudopotential calculations. We show that orthorhombic GaAs is not only metallic but also superconducting. The phase transition from GaAs II to III is a second order phase transition characterized by a continuous change in T_c. The temperature dependence of the resistivity in the normal state suggests that orthorhombic GaAs is probably an anisotropic metal whose anisotropy increases with pressure. A typical metallic density-of-states (DOS) at the Fermi level for GaAs II is obtained in our calculation from which we propose that the observed anisotropic transport is associated with an anisotropic Fermi surface.

Experiment Details and Results

The samples investigated are small chips cut from a bulk semi-insulating GaAs wafer. These samples were mounted in a gasketed diamond anvil cell using $CaSO_4$ as the pressure medium. Copper wires were pressed against the sample for quasi-four probe measurement as described in detail elsewhere.[13] The resistance of

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the sample were measured by an ac technique using a lock-in amplifier. Measurements were made either as a function of pressure at constant room temperature or as a function of temperature at almost constant pressure. In the latter experiment the sample was pressurized at room temperature and then cooled to liquid helium temperatures inside a Janis Varitemp optical dewar. The pressure inside the cell was monitored by comparing the R_1 fluorescence peak of ruby chips inside the cell near the sample and outside the cell. The pressure typically increased by less than 3 GPa as the temperature was lowered to 100 K. Below 100 K the pressure inside the cell did not change with temperature. The pressure inhomogeneity as determined by measuring the fluorescence peaks of typically four ruby chips surrounding the sample is about ±10%.

Figure 1 shows a plot of the resistance of the sample as a function of pressure at room temperature. Below 8 GPa the sample resistance was too high to be measured. The main feature of interest in Fig. 1 is the precipitous drop in the resistance beginning around 14.5 GPa. Beyond 16 GPa the resistance showed only a slight further decrease with pressure. We attribute this drop in resistance by more than five order of magnitude to the transition of GaAs from the zincblende structure to the orthorhombic structure. The pressure of this transition as determined from the resistance technique is 16 GPa. This pressure is lower than the corresponding value determined from the x-ray technique because, whenever there is a pressure distribution, the electrical resistance is dominated by the more conducting higher pressure regions.

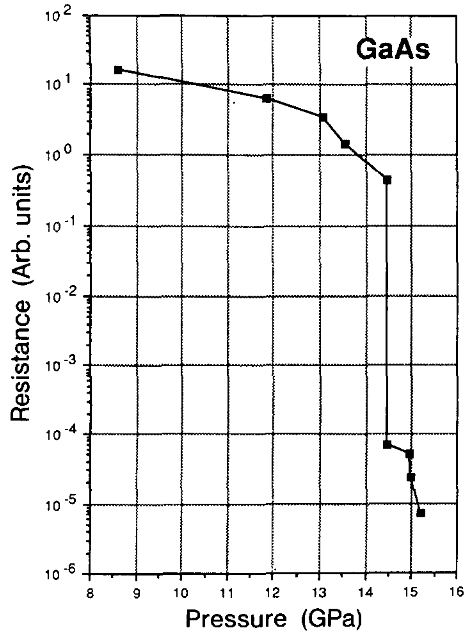

Figure 1. Resistence vs pressure at room temperature in GaAs showing the phase transition between GaAs I and GaAs II in the vicinity of 15 GPa.

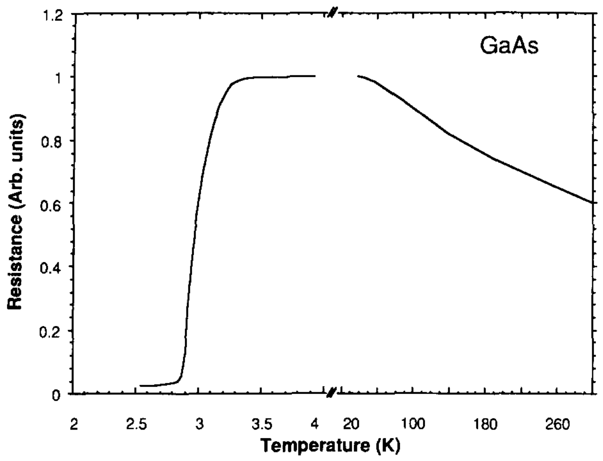

Figure 2. Resistence vs temperature of GaAs at a pressure of 40.8 GPa showing the "anomalous" increase in R for temperatures between 300 K and 50 K and also the superconductivity transition at 3 K. Note the change in the temperature scale between 20 K and 4 K.

The temperature dependence of the sample resistance has been measured as a function of temperature at several pressures between 20 GPa and 50 GPa. At pressures around 20 GPa we found that the resistance decreases with decreasing temperature like a normal metal down to about 5 K. At lower temperatures the resistance showed a sudden further decrease at 4.5 K which we identify as a superconducting transition. In the superconducting phase we found a residual resistance, presumably because of the presence of a remanent small amount of the lower pressure semiconducting phase. As pressure was increased further this residual resistance almost completely disappeared. But as the pressure was increased beyond 30 GPa we also found that the resistance in the normal state began to depend on temperature in an anomalous way. Instead of the resistance decreasing with decrease in temperature, the resistance now increased slightly as the temperature was decreased from 300 to 50 K (see Fig. 2). The resistance remained fairly constant between 50 K and the superconducting transition. The transition temperature decreased monotonically from 4.5 to below 3 K as the pressure was increased to 48 GPa. The sharpness of the transition did not change appreciably as the pressure was increased. The increase in resistance in the normal state as the temperature was lowered did not appear to be activated.

Theory and Discussions

In an attempt to understand the experimental results we have applied the pseudopotential approach[14] within a local density approximation[15] to calculate the electronic band structure of orthorhombic GaAs. Figure 3 (a) shows a typical band structure of GaAs II at 70% of the equilibrium unit cell volume which corresponds to a pressure of approximately 23 GPa.[9] According to Ref. 9, transition to another orthorhombic phase, GaAs III, occurs at about 24 GPa. This phase then transforms to GaAs IV at about 60-80 GPa. The x-ray patterns before and after the phase transitions are very similar for both the GaAs II to GaAs III transition and for the transition to GaAs IV which suggests that the crystal structure of GaAs gradually changes from GaAs II to GaAs IV. Hence, we do not expect dramatic changes in the band structure of GaAs in the pressure range of 20 - 30 GPa. The structure of GaAs II is discussed in detail in Ref. 12. In Fig. 3 (b), the corresponding one electron density-of-states is also shown.

According to the band structure in Fig. 3 (a) GaAs II is a metal with significant overlap between the conduction and valence band along the Γ-Y and Γ-Z directions. An understanding of the band structure of GaAs II can be obtained by comparing it with the corresponding band structures of GaAs with the zincblende and NaCl structures.[8,12] It was pointed out by Froyen and Cohen[8] that the NaCl structure was metallic because its conduction band state at the X point of the Brillouin zone was considerably lower than the valence band maximum at Γ. Otherwise the band structure of GaAs in the NaCl structure was quite similar to its band structure in the zincblende structure. The orthorhombic GaAs II structure can be obtained from the NaCl structure by displacing the atoms as in a transverse acoustic phonon with wave vector equal to one of the X-points of the Brillouin zone (X_z) provides that the lattice parameters are kept the same. In this transformation the Brillouin zone of the face-centered cubic (fcc) lattice is reduced to half of the original size by folding back the (001) $2\pi/a$ face to the center plane of zero k_z. The $X_{x,y}$ and L points of the fcc lattice are mapped into the Y and R points of the orthorhombic lattice. The X_z point of the fcc lattice is folded into the Γ point of the orthorhombic lattice. This results in anti-level crossings between the conduction and valence bands in several regions in the Brillouin zone (see Fig. 3 (a)) and reduces somewhat the DOS near the Fermi level. As a result the DOS at the Fermi level of the orthorhombic phase shown in Fig. 3 (b) is only 4.1 states/Ry/molecule/spin, or about 23% less than that of the NaCl structure. However, this DOS still suggests that GaAs II should be a rather typical metal and is consistent with the observed T_c of around 4 K. In comparison the DOS at the Fermi level for Ge in the high pressure β-Sn phase is about 2.1 states/Ry/atom/spin,[5] and the corresponding T_c is 5.3 K.[3]

The folding of the fcc lattice Brillouin zone of the cubic NaCl structure also suggests an an- isotropic Fermi surface. This is better visualized by comparing the real space distributions of the conduction states near the Fermi level of orthorhombic GaAs in two orthorgonal planes, the (001) and (010) planes. The results are shown in Fig. 4 where a small energy window of 0.2 eV is used. In the x-y plane, the charge distribution is typical of metallic bonding of NaCl phase. However, in the y-z plane, the charge distribution is characterized by charge pile-ups along the zigzag chains of GaAs atoms along the z-direction that are reminiscent of covalent bonds in zincblende GaAs.

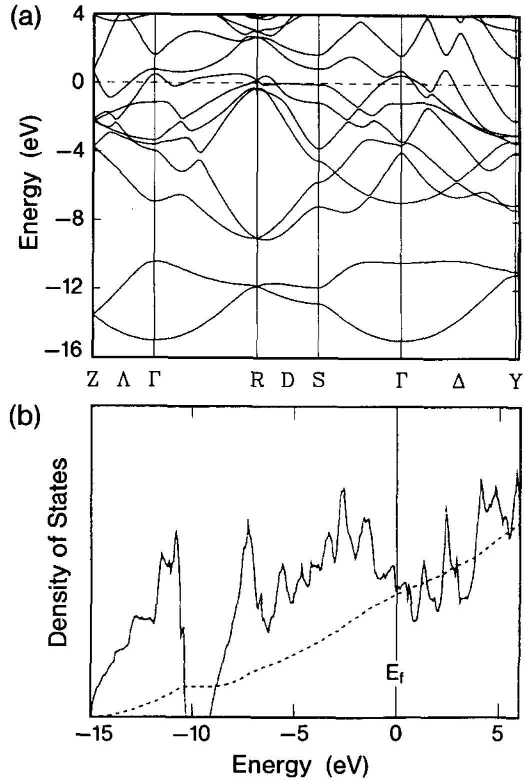

Figure 3. (a) band structures along symmetry lines of GaAs II at 70% of the equilibrium unit cell volume. The dashed line is the Fermi level. Anti-level crossings between the conduction and valence bands can be observed, e.g., around S and around two third of Λ. (b) density of states (solid line) and integrated density of states (dashed line).

The anisotropic Fermi surface would result in anisotropic transport properties which, together with sample inhomogeneity, may explain the anomalous temperature dependence of the normal state resistance in Fig. 2. We note that a similar anomalous temperature dependence has been reported in the highly anisotropic high T_c superconductors such as polycrystalline LaBaCuO[16] and LaCaCuO[17] and even in single crystalline BiCaSrCuO.[18] In case of the polycrystalline compounds, the increase in resistivity upon lowering the temperature have been explained by the existence of a mixture of metallic and insulating phases in the sample. Since we find an increase in the anomalous behavior as the pressure is increased, this seemed to rule out the possibility that our sample at over 20 GPa above the transition pressure still contained some

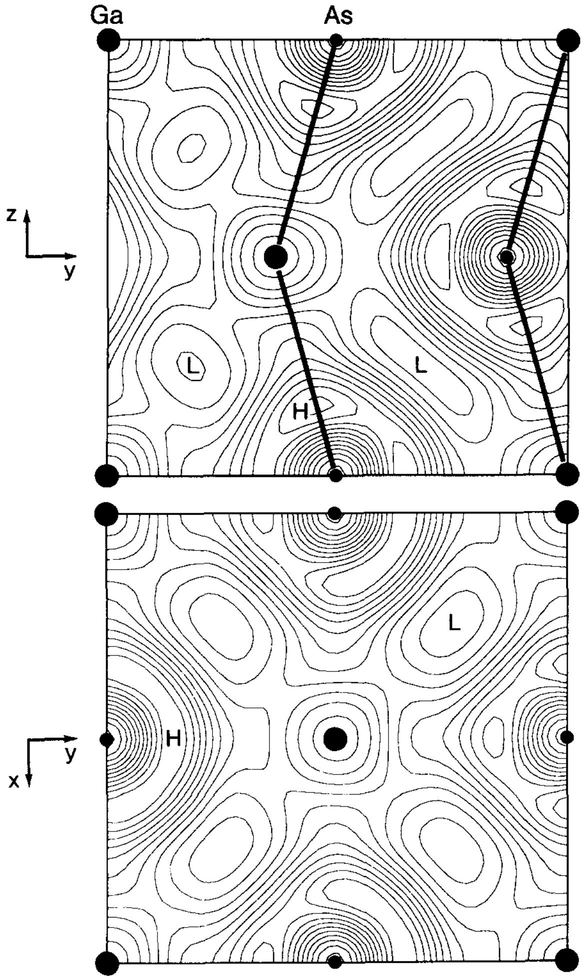

Figure 4. Charge contour plots for GaAs II in the x-y plane (lower panel) and y-z plane (upper panel), respectively. The volume is the same as in Fig. 3.

low-pressure semiconducting phase. Instead, we believe that the anomalous temperature dependence of the resistivity may be associated with defects at dislocations or grain boundaries. Although our starting sample was single crystalline, it was most likely polycrystalline with probably a fairly large amount of defects induced by the two structural phase transitions from GaAs I to GaAs II and then to GaAs III. It is well-known that resistance in highly disordered metals and doped semiconductors can increase as temperature is decreased due to carrier localization.[19] So far such localization effects have been observed typically at low temperatures. However, it is possible that they may be observable at higher temperatures due to the anisotropic Fermi surfaces in orthorhombic GaAs. For example, if the density of states at the Fermi surface along the z axis is low enough, then localization effects due to defects may set in even at room temperature. The exact shape of the resistance anomaly would be determined by the orientation of the crystallites. It is possible that at higher temperature the effects due to localization along the z axis dominates, while at low enough temperature the nornal metallic and superconducting behavior in the x-y plane shorts out the more resistive crystallites oriented along the z direction. For a detailed study of these properties, the structure of GaAs III for pressure above 30 GPa is now being investigated and results will be discussed in a separate paper.[20]

Conclusion

We have demonstrated for the first time that the high pressure phases of GaAs are superconducting with transition temperatures comparable to those predicted for the corresponding covalent element Ge. Hence, it is expected that the ionicity of GaAs does not greatly influence the metallic properties of its high pressure phases. We expect that other III-V semiconductors will also become metallic and superconducting in their high pressure phases.

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References

1. S. Minomura and H.G. Drickamer, J. Phys. Chem. Solids 23, 451 (1962).
2. H. Olijnyk, S.K. Sikka and W.B. Holzapfel, Phys. Lett. 103A, 137 (1984); M.T. Yin and M.L. Cohen, Phys. Rev. B 26, 5668 (1982); K.J. Chang and M.L. Cohen, Phys. Rev. B 34, 8581 (1986), and references therein.
3. J. Wittig, Z. Phys. 195, 215 (1966).
4. D. Erskine, P.Y. Yu, K.J. Chang, and M.L. Cohen, Phys. Rev. Lett. 57, 2741 (1986).
5. K.J. Chang and M.L. Cohen, Phys. Rev. B 34, 4552 (1986).
6. S.C. Yu, I.L. Spain, and E.F. Skelton, Solid State Commun. 25, 49 (1978).
7. M.A. Baublitz and A.L. Ruoff, J. Appl. Phys. 53, 6179 (1982).
8. S. Froyen and M.L. Cohen, Phys. Rev. B 28, 3258 (1983).
9. S.T. Weir, Y.K. Vohra, C.A. Vanderborgh, and A.L. Ruoff, Phys. Rev. B 39, 1280 (1989).

10. S.B. Zhang and M.L. Cohen, Phys. Rev. B 35, 7604 (1987).
11. S.T. Weir, Y.K. Vohra, and A.L. Ruoff, Phys. Rev. B 36, 4543 (1987).
12. S.B. Zhang and M.L. Cohen, Phys. Rev. B 39, 1450 (1989).
13. D. Erskine, P.Y. Yu and G. Martinez, Rev. Sci. Instrum. 58, 406 (1987).
14. M.L. Cohen, Phys. Scr. T1, 5 (1982).
15. *Theory of Inhomogeneous Electron Gas*, edited by S. Lundqvist and N.H. March (Plenum, New York, 1983), and references therein.
16. J.G. Bednorz and K.A. Müller, Z. Phys. B 64, 189 (1986).
17. J.G. Bednorz, K.A. Müller and M. Takashige, Science, 236, 73 (1987).
18. S. Martin, A.T. Fiory, R.M. Heming, L.F. Schneemeyer and J.V. Waszezak, Phys. Rev. Lett. 60, 2194 (1988).
19. N.F. Mott and E.A. Davis, *Electronic Processes in Noncrystalline Meterials*, 2nd ed. (Claredon Press, Oxford, 1979).
20. A. Garcia, S.B. Zhang and M.L. Cohen, (unpublished).