

Valence charge density in InSb

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(Received 19 February 1985)

Valence charge densities in InSb have been calculated at several volumes using an *ab initio* pseudopotential method. From these the x-ray structure factors $F(222)$ and $F(\bar{2}\bar{2}\bar{2})$ at 0 K were calculated. It is found that these do not show any rapid variation near the transition, indicating that experimental results showing a sharp decrease in these structure factors just before the transition are very likely due to an anharmonic effect and not a charge redistribution.

InSb is an interesting material with potentially important device applications. Over a relatively small range of pressures and temperatures, it is found to occur in a number of structures.¹ Moreover, amorphous InSb has been observed to transform to a metastable NaCl type structure under pressure at room temperature.² The extent of this polymorphism may be interpreted as suggesting that InSb is a borderline material with a near instability in its bonding. It seems reasonable that substantial insights into the nature of covalently bonded materials may be obtained from the study of such materials and their similarities with, and differences from, prototypical materials such as silicon.

Recently Yoder-Short, Colella, and Weinstein³ have experimentally studied the behavior of the valence electron densities under pressure for both InSb and Si using x-ray diffraction. They observed that as the pressure was increased to the transition pressure, the two materials displayed similar behavior. In both cases the intensity of the quasiforbidden (222) reflection, which is associated with the valence electrons,⁴ fell off sharply just below the transition pressure. Two interpretations of this observation were offered. First, it was suggested that the valence electrons may have redistributed just before the transition pressure; this redistribution destabilizing the tetrahedrally coordinated structures and leading to the transition. The second interpretation offered was that the decrease in the intensity may not have been associated with a redistribution of the charge density away from the covalent bonds but rather with an anharmonic effect. It was proposed that the transition might be associated with a soft-phonon mode which also

yields the change in the scattering factors. This would explain the association of the reduction in the structure factor and the transition pressure.

Subsequent to the experimental study, Yin and Cohen⁵ calculated the valence electron density of silicon under pressure using an *ab initio* pseudopotential method. They found that the bond charge does not show any sharp decrease about the transition pressure, at least for silicon. As yet, however, the exact cause of the experimental observation has not been established.

In this Brief Report, we present calculated charge densities and x-ray structure factors for InSb at a variety of volumes. These were calculated using a density-functional method with a plane-wave basis.⁶ The pseudopotentials used were those tabulated by Bachelet, Hammann, and Schlüter.⁷ The calculations were done using a set of two special points⁸ in the irreducible wedge of the Brillouin zone and about 530 plane waves. Increasing the number of plane waves to 725 at the experimental-free volume Ω_0 was found to change the lower Fourier components of the charge density by less than 2×10^{-3} electrons per cell. In Table I we give the first few Fourier components of the valence charge density at the free volume. These are compared with the results of an earlier calculation by Chelikowski and Cohen.⁹ In spite of the fact that they used an empirical pseudopotential and only about 90 plane waves in their calculation, it will be observed that the results of their calculation agree fairly well with ours. In Table II we present values of $F(222)$ and $F(\bar{2}\bar{2}\bar{2})$ for Cu $K\alpha$ radiation at a variety of volumes Ω . The ionic scattering factors used were from

TABLE I. Fourier components of the charge density (e/Ω_0) for InSb in the ZnS structure. The origin is at the cation site.

G	Fourier components			
	Ref. 9	This calculation		
111	0.994	-1.915	0.846	-1.882
200	-0.718	0	-0.766	0
220	0.144	0	-0.024	0
311	-0.223	-0.161	-0.227	-0.267
222	0.020	-0.409	0.091	-0.252
400	-0.245	0	-0.467	0
331	0.045	0.038	-0.054	0.223
420	0.048	0	0.152	0
422	-0.043	0.024	-0.235	0.015

TABLE II. X-ray structure factors in InSb in the ZnS structure for Cu $K\alpha$ radiation.

Ω/Ω_0	$F(222)$	$F(\bar{2}\bar{2}\bar{2})$
1.035	6.41	5.23
1.000	6.42	5.26
0.985	6.42	5.26
0.938	6.44	5.29
0.892	6.45	5.33
0.847	6.46	5.37
0.804	6.48	5.41
0.762	6.49	5.46
0.722	6.50	5.51
0.646	6.51	5.61

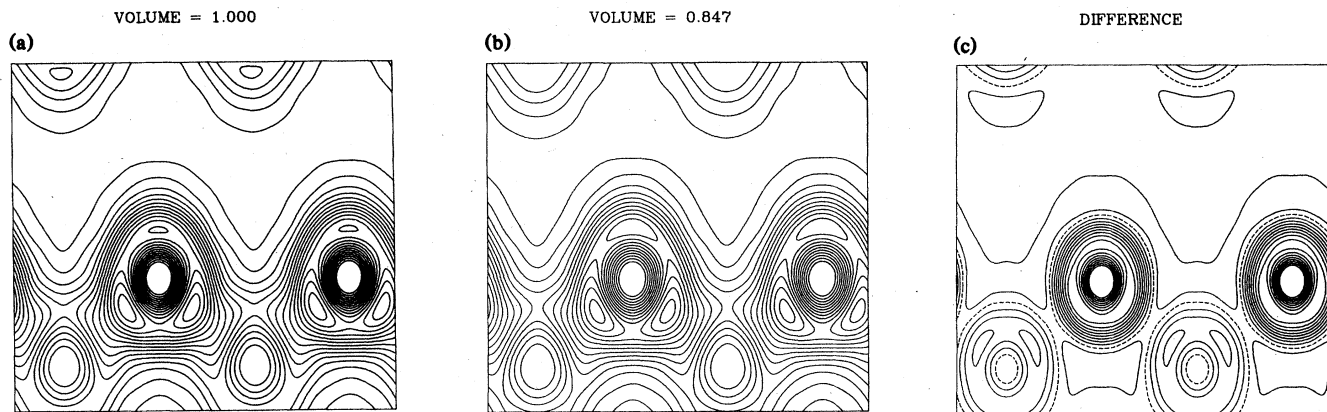


FIG. 1. (110) charge densities at (a) $\Omega/\Omega_0=1$ and (b) $\Omega/\Omega_0=0.847$, and (c) the difference (a) - (b) in electrons per cell. Adjacent contours are separated by 2 electrons/cell in (a) and (b), and 0.5 electrons/cell in the difference. The dashed contour is at zero. For InSb the transition occurs at about $\Omega/\Omega_0=0.945$.

Hartree-Fock calculations.^{10,11} It will be observed that the free volume results are in good agreement with the 0 K experimental values of Ref. 4.

In Fig. 1 contour plots of the valence charge densities at Ω_0 and at $\Omega/\Omega_0=0.847$ are presented for a (110) section. The difference is also shown. The results are qualitatively very similar to those obtained for silicon in Ref. 5.

From the results presented in Table II, one may note that there is no evidence for a dramatic redistribution of the

valence charge density near the transition volume or even at volumes much smaller than it and, moreover, from Fig. 1(c) that the redistribution which does occur is mainly spherical about the ions. This result implies that the experimentally observed drop in the x-ray structure factors is very likely an anharmonic effect.

This work was supported by the Natural Sciences and Engineering Research Council of Canada.

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