# Lattice Constant at the Insulator-Metal Transition of Crystalline Xenon

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(Received 22 July 1980)

The metallization lattice constant for fcc Xe has been calculated in three different, independent ways. The result is relatively insensitive to basis set, details of local exchange-correlation potential, or use of the muffin-tin potential. The calculated metallization lattice constant is 7.9 a.u. or $P = 1.28$ Mbar, confirming Ross and McMahan's calculation but disagreeing with Nelson and Ruoff's experimental value.

PACS numbers: 71.30.+h, 64.30.+t, 71.25.Tn

Metallic conduction in Xe at 330 kbar and 32 K has been reported by Nelson and Ruoff.[1] Subsequently, Ross and McMahan[2] reported an augmented-plane-wave calculation (APW) with Hedin-Lundquist local exchange and correlation. They found no metallization until $P = 1.3$ Mbar, a result confirmed by Worth and Trickey[3] and by Wilkins and Williams.[3] In view of the fact that simple local-density theories always give a smaller band gap at $P = 0$ than the experimental value,[4] it is quite surprising that the calculated metallization pressure is almost a factor of 4 greater than that reported from experiment. It is especially surprising in view of the excellent agreement[2,5] between calculated and measured $P$-$V$ curves over the entire pressure range. We have therefore undertaken an extensive check to see whether we could uncover any flaw in the pressure calculations.

Our first concern was muffin-tin effects introduced by the standard implementation of the APW formulism, as well as related effects in the newly developed augmented-spherical-wave method[6] used by Wilkins and Williams (Ref. 3). Recently two of us (A.K.R. and S.B.T.) have developed a computer code which enables one to use our self-consistent, muffin-tin APW output as input to the Wang-Calloway[7] linear combination of Gaussian-type orbitals (LCGTO) code. We are enabled thus to assess muffin-tin effects by direct, systematic calculations. The LCGTO *Ansatz* opens up the possibilty of basis-set inadequacies, of course. We have attempted to confront that problem in two ways. First, we have chosen a rather large Gaussian basis (16 $s$, 12 $p$, 8 $d$) of Huzinaga.[8] Second, we have used the local orbitals, mixed basis (Slater-type orbitals plus plane waves, hereafter STO + PW) scheme of Kunz.[9] Here we used STO basis set contracted to $5s$, $4p$, $2d$ functions plus 113 plane waves. Our third concern was with the details of the local-exchange-correlation model employed. To probe this possible source of discrepancy with experiment, we did the APW and LCGTO calculations using $X\alpha$ exchange-correlation with the so-called virial-theorem $\alpha$,[10] while the STO + PW calculation used the Kohn-Sham-Gaspar (KSG) value of $\alpha$ plus a self-energy correction.[11] All calculations were done on a 256-point first-Brillouin-zone mesh.

Neither the LCGTO nor the STO + PW computer codes are equipped at present to compute total energies and hence $T = 0$ K static lattice $P$-$V$ curves. Therefore, we have tabulated our data as a function of the cubic lattice constant and used the APW-$X\alpha$ equation of state to convert to a corresponding pressure (see Table I). Since it is well established[2,5] that the APW-$X\alpha$ equation of state matches a wide variety of experimental data quite well, our utilization of it seems quite reasonable.

The tabulation shows clearly that there is no technical aspect (muffin tin, basis set, local exchange-correlation details) to which the discrepancy between theory and experiment can be traced, unless one assumes a drastically different relation between lattice constant and pressure. Apparently there are strong non-muffin-tin corrections to the APW-$X\alpha$ formulism which manifest themselves in appreciable shifts of the calculated gap when the LCGTO input is the APW-$X\alpha$-converged results. These shifts obviously do not reduce the discrepancy with experiment; rather, they enlarge it!

The three calculations are mutually consistent, in that the simple $X\alpha$ model, as expected, gives

TABLE I. Calculated Xe band gaps (see text for notation).

| $a$ (bohr) | $V$ (cm$^3$/mole) | Energy gaps (Ry)<br>APW $X\alpha$ | <br>LCGTO $X\alpha$ | <br>STO + PW | APW-$X\alpha$ pressure (kbar) |
|---|---|---|---|---|---|
| 11.6194 | 34.9983 | 0.4517 | 0.4601 | ⋯ | 0.319 |
| 11.3760 | 32.8447 | ⋯ | ⋯ | 0.75 | ⋯ |
| 8.9511 | 15.9943 | 0.2320 | 0.4438 | 0.50 | 331.9 |
| 7.9001 | 11.0000 | 0.0023 | − 0.0180 | 0.12 | 1275.8 |

gaps that are smaller than the KSG plus self-energy correction scheme. The KSG exchange-correlation by itself (i.e., $X\alpha$ with $\alpha = \frac{2}{3}$) would give a smaller gap than the $X\alpha$ with virial-theorem $\alpha$.[4] However, the specific self-energy correction term employed along with the KSG term is such as to effect a cancellation of Coulombic self-energies correctly but to leave exchange-correlation self-energy cancellation at an approximate level. The obvious result is that interelectron repulsion is reduced and the band gap is enlarged.

A possible source of the discrepancy between theory and experiment might be relativistic corrections. The effect of such correction on the calculated band gap is known, however, to be quite small. For example, in NaI the nonrelativistic band gap is calculated as 0.42 Ry while the relativistic gap is 0.43 Ry.[12] Thus, the primary effects of relativistic corrections are felt by the deep core states. The effects on valence and conduction states are much too small to reduce the calculated band gaps at about 16 cm$^3$/mole essentially to zero, as would be required to bring theory and experiment into agreement.

It is also difficult to envisage any crystallographic phase change which would drive an insulator-metal transition in Xe. The equilibrium phase is after all fcc and it seems most implausible that compressing such a crystal could cause any quasi Mott transition to a less-than-close-packed structure (whose Brillouin zone then corresponded to band overlap). Virtually the only plausible alternative phase is hcp. It is difficult in the extreme to see how a phase change from fcc to hcp would cause a gap reduction of the order of 0.3–0.5 Ry, since the typical fcc-hcp free-energy difference (at $P = 0$) is known to be only a few $\mu$Ry.[13]

In any event, it should be noted that the simplest model, APW $X\alpha$, has been quite successful in dealing with the bcc-fcc transition in $^{14}$Cs and with the metal-semimetal-metal sequence in Ca.[15] These successes, plus the mutual consistency of all the energy band work to data on Xe metallization lead us reluctantly to the conclusion that some aspect of the experiment has been interpreted incorrectly. Two possibilities are (1) undetected difficulties or ambiguities with the pressure scale; (2) nonuniform strains which generate a closely spaced manifold of defect states in the band gap. Whatever the validity of these speculations, we believe that further theoretical and computational effort will not be very fruitful without careful reexamination and, if possible, replication of the experiment which prompted this effort.

A portion of this work was completed while one of us (S.B.T.) was a visitor in the Materials Research Laboratory of the University of Illinois, for which he also thanks R. O. Simmons. Computational support for two of us (A.K.R. and S.B.T.) from the North East Regional Data Center of the State University System of Florida is acknowledged with thanks. This work was supported in part by the National Science Foundation under Contract Nos. DMR-78-24155 and DMR-79-09721.

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# Frequency-Dependent Conductivity in NbSe$_3$

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(Received 27 March 1980)

The observation of a frequency-dependent conductivity ($\sigma$) and dielectric constant ($\epsilon$) in NbSe$_3$ is reported. In both charge-density–wave phases a strong frequency dependence and huge dielectric constant are observed below 100 MHz, with greatest effects observed at 42 K. The conductivity $\sigma$ increases smoothly from the dc value to the high-frequency ($f = 100$ MHz) limit; this increase is accompanied by the reduction of $\epsilon$. A resistance-capacitance network model is suggested to account for the observed frequency dependence.

PACS numbers: 72.15.Nj, 72.15.Eb, 72.30.+q, 72.60.+g

Niobium triselenide, NbSe$_3$, shows two phase transitions,[1] at 145 K ($T_1$) and 59 K ($T_2$) associated with the development of incommensurate charge-density waves (CDW). These transitions lead to the increase of resistivity which is ascribed to the reduction of the Fermi surface;[2,3] the CDW condensate is assumed to be pinned by impurities to give negligible contribution to the dc conductivity at low electric fields. The conductivity increases when the electric field is larger than a threshold field $E_T$ and then saturates at high electric fields.[4-6] This and the observation of noise in the nonlinear region[6,7] together with the x ray observation of the superstructure at high electric fields[8] demonstrate that the depinning of the CDW is responsible for the increase of the conductivity with increasing electric field. The resistive anomalies are also suppressed at microwave frequencies[2] suggesting that the pinning frequency is less than $10^{10}$ Hz.

In this paper we report the first observation of frequency-dependent conductivity associated with the incommensurate CDW states in NbSe$_3$. We show that the CDW anomalies are suppressed at extremely low frequencies and also lead to a gigantic dielectric constant. The transition between the low-frequency ($f < 1$ MHz) and high-frequency ($f > 100$ MHz) limit is smooth with no clearcut evidence for a well-defined pinned CDW mode.

The conductivity was measured between 10 and 300 K by a two-probe configuration. Contact resistances, measured by dc four-probe configuration, were found to be two orders of magnitude smaller than the sample resistance. Also the measured resistance (including the small contact resistance contribution) was found to be independent of frequency in the high temperature, metallic region showing that the measured frequency dependence at low temperatures is associated with the behavior of NbSe$_3$. A bridge method was used up to 100 MHz and a radiofrequency circulator circuit at high frequencies.[9] In both cases the sample impedance is represented by a parallel *RC* circuit which is balanced by variable resistance and capacitance components. The balance of the resistive component gives $\mathrm{Re}\sigma(\omega) = R^{-1}$, the balance of the capacitance gives $\mathrm{Im}\sigma(\omega) = C$ with the dielectric constant defined as $\epsilon(\omega) = \mathrm{Im}\sigma(\omega)/\omega$. Our measuring configuration allows the joint measurement of the dc and rf conductivity. $\mathrm{Re}\sigma(\omega)$ can be measured with an accuracy better than a few percent, but the balancing out of the phase component is more ambiguous: values of $\mathrm{Im}\sigma(\omega)$ have an error of about 30%. Measurements up to 100 MHz were performed on