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PHYSICAL REVIEW B VOLUME 1, NUMBER 12 15 JUNE 1970

# Ionized-Impurity-Limited Mobility of $\alpha$-Sn in the Random-Phase Approximation*

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(Received 29 January 1970)

A calculation of the ionized-impurity-limited mobility of a $\Gamma_8$ conduction band is performed, using a random-phase-approximation dielectric function and taking into account the effects of band nonparabolicity and $p$-like character of the wave function on the scattering calculation. The results are compared with measured mobilities of Sb-doped $\alpha$-Sn. It is shown that, assuming singly ionized donor impurities, the calculated results are grossly larger than the experimental values. The results are somewhat better for doubly ionized impurities. It is pointed out that the results of a calculation using a concentration-independent dielectric constant are in excellent agreement with experiment over the whole range of accessible concentration. These results indicate that, if the impurities are singly ionized Sb, the random-phase approximation considerably overestimates the interband polarization.

## I. INTRODUCTION

$\alpha$-Sn is the allotrope of tin with the diamond crystal structure. Its electron band structure is similar to that of other diamond structure members of column IV, except that the $s_{1/2}$-like $\Gamma_6^-$ level is depressed so as to lie between the $p_{3/2}$-like $\Gamma_8^+$ level and the $p_{1/2}$-like $\Gamma_7^+$ level.[1] Part of the fourfold-degenerate $\Gamma_8^+$ band then becomes a conduction band and part a valence band. The closest lying band extremum, $L_6^+$, lies slightly above $\Gamma_8^+$, and thus the material becomes a perfect semimetal with a symmetry-induced degeneracy of the valence-band maximum and conduction-band minimum. For this reason, it has been the subject of considerable interest as a candidate for an excitonic phase transition.

However, Liu and Brust,[2] using the random-phase approximation, showed that, because the degeneracy of the band edges is symmetry induced, the static dielectric function $\epsilon(q)$ diverges like $q^{-1}$ as $q \rightarrow 0$. The presence of impurity carriers is sufficient to remove this divergence through Thomas-Fermi screening, leaving a finite interband part which is strongly dependent on impurity carrier concentration. Liu and Tosatti[3] calculated the concentration-dependent dielectric function in the random-phase approximation and showed that the resulting ionized-impurity-limited mobilities were in excellent agreement with the anomalously large values[4,5] observed in degenerate $n$-type samples.

Liu and Tosatti, in their scattering calculation, treated the conduction electrons as $s$-like with a parabolic dispersion relation. However, $\alpha$-Sn conduction electrons are $p$-like, and there are considerable differences between the scattering cross sections of $s$- and $p$-like electrons.[6] Differential scattering cross sections for large-angle scattering of $p$-like electrons are much smaller than those for $s$-like electrons. This is especially important in a mobility calculation because the Boltzmann equation heavily weights large-angle scattering. In addition, the $\alpha$-Sn conduction-band dispersion relation is quite nonparabolic, the effective mass at the Fermi surface changing by 30% in the concentration range considered by Liu and Tosatti. Since the density of states enters the mobility calculation squared, the nonparabolicity is quite important. A calculation was performed[7] which showed that excellent agreement could be obtained with the observed mobilities,[4,5] using a concentration-independent background dielectric constant and taking into account the $p$-like character of the wave function and the nonparabolicity of the conduction-band dispersion relation.

It was estimated[7] that if one also included the interband polarization, as calculated with the random-phase approximation, the results would be roughly four times as large as the measured mobilities[4,5] at low concentrations.

In this paper, we will perform such a calculation. In Sec. II, the dielectric function for the nonparabolic band structure will be examined in the random-phase approximation. In Sec. III, expressions for the mobility will be derived, and in Sec. IV these will be compared with experiment.

The band-theory framework of this calculation is the Kane[8] three-band model, in which the shape of the band is determined by the $\vec{\mathrm{k}}\cdot\vec{\mathrm{p}}$ interaction of $\Gamma_6^-$, $\Gamma_8^+$, and $\Gamma_7^+$. The parameters of the theory are $E_g$ ($\Gamma_8^+ - \Gamma_6^-$ splitting), $\mu$ (the zone-center cyclotron mass ratio), and $\Delta$ (the $\Gamma_{25'}^+$ spin-orbit splitting). These have been measured for α-Sn by Groves *et al.*[9] The notation is the same as Kane's,[8] except that our $E_g$ is the negative of his. The only other quantity needed for the calculation is the background dielectric constant $\epsilon_0$, which has been measured by Lindquist and Ewald.[10]

## II. DIELECTRIC FUNCTION

The random-phase-approximation expression[11] for the static dielectric function $\epsilon(q)$ is

$$\epsilon(q) = 1 - \frac{4\pi e^2}{q^2} \sum_{n,n',\vec{\mathrm{k}}} \frac{|\langle\vec{\mathrm{k}},n|e^{-i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}}|\vec{\mathrm{k}}+\vec{\mathrm{q}},n'\rangle|^2}{E_{\vec{\mathrm{k}}+\vec{\mathrm{q}},n'} - E_{\vec{\mathrm{k}},n}}$$

$$\times (N_{\vec{\mathrm{k}}+\vec{\mathrm{q}},n'} - N_{\vec{\mathrm{k}},n}) \quad . \tag{1}$$

$N_{\vec{\mathrm{k}},n}$ is the probability that the state $|\vec{\mathrm{k}},n\rangle$ is occupied. This may be separated as follows:

$$\epsilon(q) = 4\pi\alpha^{\mathrm{intra}} + \epsilon_I(q) \quad , \tag{2}$$

$$4\pi\alpha^{\mathrm{intra}} = k_{\mathrm{TF}}^2/q^2 \quad , \tag{3}$$

$$\epsilon_I(q) = 4\pi\alpha^{\mathrm{inter}} + \epsilon_0 \quad . \tag{4}$$

$4\pi\alpha^{\mathrm{intra}}$ is the contribution from the conduction band, the ordinary Thomas-Fermi screening. $\epsilon_I(q)$ is the interband contribution, which is itself separated into two parts. $4\pi\alpha^{\mathrm{inter}}$ is the contribution from the overlap of the $\Gamma_8$ conduction-band wave function on the $\Gamma_8$ valence-band wave function, and $\epsilon_0$ is the contribution from all other bands.

Liu and Tosatti[3] have evaluated $4\pi\alpha^{\mathrm{inter}}$ for nonzero impurity carrier concentrations, using the matrix element obtained by Liu and Brust,[2]

$$|M_{\mathrm{LB}}|^2 = |\langle\vec{\mathrm{k}},c|e^{-i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}}|\vec{\mathrm{k}}+\vec{\mathrm{q}},v\rangle|^2$$

$$= \frac{3}{4}\,\frac{q^2\sin^2\theta}{k^2+q^2+2kq\cos\theta} \quad , \tag{5}$$

where $\theta$ is the angle between $\vec{\mathrm{k}}$ and $\vec{\mathrm{q}}$. They obtain the expression

$$4\pi\alpha^{\mathrm{inter}} = \frac{6e^2\mu m_0}{\pi\hbar^2 k_F}\left(F(q) - \frac{k_F q}{4K^2}\right) \quad , \tag{6}$$

where $\mu$ is the effective-mass ratio, $k_F$ is the Fermi momentum, and $K$ is the average radius of the first Brillouin zone. The second term in the bracket is very small, and the function $F(q)$, which is independent of the characteristics of the material, is well approximated by

$$F(q) = \tfrac{4}{3}[1 - a'(q/k_F)^2] \quad , \tag{7}$$

with $a' \approx \frac{1}{12}$. In deriving the expression (6), they made use of the parabolic dispersion relation.

One can directly evaluate $4\pi\alpha^{\mathrm{inter}}$ for the nonparabolic band structure by numerical integration of (1). The results are very cumbersome and yield no simple universal function like $F(q)$ for the $q$ dependence. Equation (6) would be very attractive for use in the scattering calculation because of its simple analytical form, but at first glance it would appear to be quite inaccurate because the parabolic dispersion relation used in its derivation differs markedly from that of the nonparabolic model. However, the matrix element of the nonparabolic model

$$|M|^2 = |\langle\vec{\mathrm{k}},c|e^{-i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}}|\vec{\mathrm{k}}+\vec{\mathrm{q}},v\rangle|^2 \tag{8}$$

also differs from the Liu-Brust matrix element because the $p$-like component of the conduction-band wave function decreases as one moves away from the zone center. Using $\vec{\mathrm{k}}\cdot\vec{\mathrm{p}}$ theory[8] one can show, if one ignores the mixing of other bands into the $\Gamma_8^+$ valence band (which is quite reasonable since its effective mass is very high), that the correct matrix element is given by

$$|M|^2 = \tfrac{1}{3}[(b_k + \sqrt{2}\,c_k)^2]\,|M_{\mathrm{LB}}|^2 \quad , \tag{9}$$

where $$b_k = (\sqrt{3})^{-1}(\xi_k + 1)/N \quad , \tag{10}$$

$$c_k = \sqrt{(\tfrac{2}{3})}(\xi_k + 1)(\tfrac{3}{2}\delta\xi_k + 1)/N \quad , \tag{11}$$

$$a_k = [\xi_k(\xi_k + 1)(\delta\xi_k + 1)(\tfrac{3}{2}\delta\xi_k + 1)]^{1/2}/N \quad . \tag{12}$$

Here $N$ is the square root of the sum of squares of the numerators of (10), (11), and (12), $\xi_k = E_{k,c}/E_g$ and $\delta = E_g/\Delta$, where $E_g$ is the $\Gamma_8^+ - \Gamma_6^-$ splitting and $\Delta$ is the $\Gamma_{25'}^+$ spin-orbit splitting. Thus, if one wishes to compare the contribution from a region of $k$ space to $\alpha^{\mathrm{inter}}$ in the degenerate limit for the parabolic and nonparabolic models, the quantity to be examined is $\frac{1}{3}(b_k + \sqrt{2}\,c_k)^2/[E_{k,c}(\mathrm{NP})/E_{k,c}(\mathrm{P})]$, where P and NP indicate parabolic and nonparabolic, respectively.

This quantity is displayed in Fig. 1 as a function of $k^3/3\pi^2$. The numbers on the abscissa are then the electron densities if the Fermi sphere lies at $k$. As can be seen, the two effects, decrease of $p$-like component of the wave function and flatten-

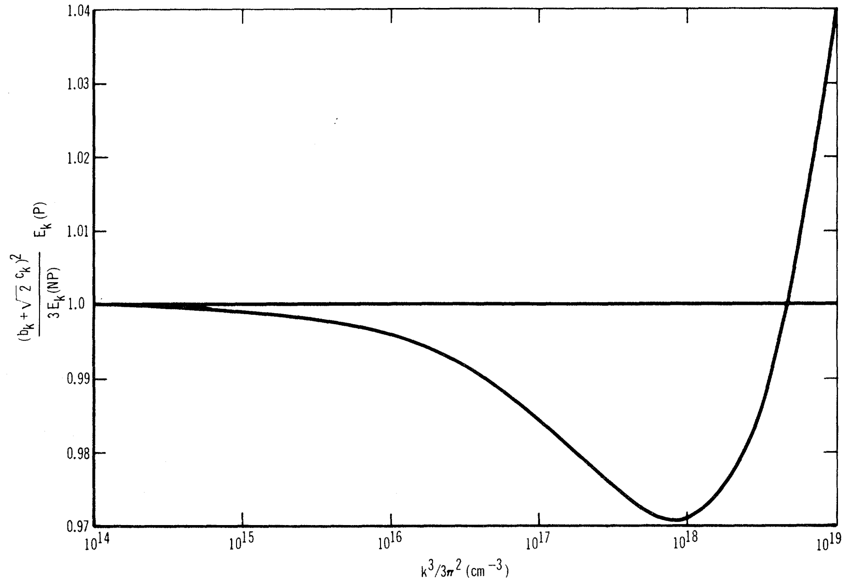

FIG. 1. Ratio of the contribution to the interband polarization from a region of $k$ space lying $k$ from the zone center for the nonparabolic band structure to that for the parabolic band structure as a function of $k^3/3\pi^2$.

ing of the dispersion relation, nearly cancel, and the contributions to $\alpha^{\text{inter}}$ are within a few percent of one another for the two models, even at crystal momenta corresponding to $10^{19}$ electrons/cm$^3$. Since most of the contribution comes from the region just outside the Fermi surface, at low concentrations, where interband polarization is especially important, Eq. (6) will be practically exact. Even at high concentrations the error should not be more than 3%, and this is insignificant since $4\pi\alpha^{\text{inter}}$ always appears added to the much larger (at high concentration) background dielectric constant $\epsilon_0$. Thus, Eq. (6) will be used to evaluate the interband polarization throughout the scattering calculation, with $\mu$ regarded as the zone-center cyclotron mass ratio.

## III. MOBILITY

We proceed with the scattering calculation in the same manner as in Ref. 6, except that we employ the bare Coulomb potential and the interband polarization of Eq. (6). The collision term of the Boltzmann equation for this scattering mechanism in the presence of an external electric field is, in the first Born approximation,

$$\left(\frac{\partial f(\vec{\mathrm{k}})}{\partial t}\right)_{\text{coll}} = \frac{\pi N_i Z_i^2}{\hbar^4}\,\frac{e^4}{\epsilon_I^2(0)}\,(2\mu m_0)^{3/2} \times E_g^{1/2}\,\frac{\lambda(\xi)}{k^3}\,\frac{\partial f_0(E)}{\partial E}\,\Phi c(E)\cos\alpha \ , \qquad (13)$$

where
$$\lambda = [\xi(\xi+1)(\delta\xi+1)/(\tfrac{3}{2}\delta\xi+1)^3]^{1/2} \times[(\xi+1)(\delta\xi+1)+\xi(\delta\xi+1)+\delta\xi(\xi+1) - \delta\xi(\xi+1)(\delta\xi+1)/(\delta\xi+\tfrac{2}{3})] \ , \qquad (14)$$

$$\Phi = \int_{-1}^{1}\frac{(1-x)}{[Ax^2+Bx+C]^2} \times \tfrac{1}{2}\sum_{\mu\mu'}\left|\int_{\text{cell}}\chi^{*}_{\vec{\mathrm{k}}\mu}\chi_{\vec{\mathrm{k}}'\mu'}\,d^3r\right|^2 dx \ , \qquad (15)$$

$$A = -2(k/k_F)^2[1-\epsilon_0/\epsilon_I(0)]\,a' \ , \qquad (16)$$

$$B = -1+4(k/k_F)^2[1-\epsilon_0/\epsilon_I(0)]\,a' \ , \qquad (17)$$

$$C = (1/2k^2)\big(k_{\text{TF}}^2/\epsilon_I(0)+2k^2 \times\{1-2(k/k_F)^2[1-\epsilon_0/\epsilon_I(0)]\,a'\}\big) \ , \qquad (18)$$

$$\frac{k_{\text{TF}}^2}{\epsilon_I(0)} = \frac{4e^2(2E_g)^{1/2}}{\pi\epsilon_I(0)}\left(\frac{\mu m_0}{\hbar^2}\right)^{3/2} \times\left(\lambda^{1/2}(\xi_F)+\eta\frac{d\lambda}{d\xi_F}(\xi_F)\right)^2 \ , \qquad (19)$$

$$\eta = [Z_i e^3/2\pi^{1/2}\epsilon_I^{3/2}(0)](\mu m_0/2E_g\hbar^2)^{3/4} \ , \qquad (20)$$

and $c(E)$ is defined by

$$f(\vec{\mathrm{k}}) = f_0(E) - kc(E)\cos\alpha\,\frac{\partial f_0(E)}{\partial E} \ . \qquad (21)$$

In these expressions $\alpha$ is the angle between $\vec{\mathrm{k}}$ and the electric field, $x$ is the cosine of the angle between $\vec{\mathrm{k}}$ and $\vec{\mathrm{k}}'$, $\chi_{\vec{\mathrm{k}}\mu}$ is the cell-periodic part of the conduction-band wave function, $f(\vec{\mathrm{k}})$ is the perturbed distribution function, $f_0(E)$ is the unperturbed distribution function, $N_i$ is the number per cm$^3$ of ionized impurities, $Z_i e$ is their charge, $\xi_F = E_F/E_g$, and $\mu$ is the zone-center effective-mass ratio. The function $\lambda(\xi)$ is proportional to the density of states per unit energy. In the degenerate limit, this Boltzmann equation yields the conductivity

$$\sigma=\frac{6\pi}{\hbar}\left(\frac{\hbar^2}{2\mu m_0}\right)^3\frac{\epsilon_I^2(0)}{e^2E_g}\frac{n_e}{Z_i}\frac{k_F^2}{\lambda^2(\xi_F)\Phi(k_F)}\ , \tag{22}$$

where $n_e$ is the number of electrons per cm$^3$.

Using $\vec{k}\cdot\vec{p}$ theory,[8] the overlap integral involving the cell-periodic parts of the wave function in Eq. (15) can be evaluated. One finds

$$\frac{1}{2}\sum_{\mu\mu'}\left|\int_{\text{cell}}\chi^*_{\vec{k}\mu}\chi_{\vec{k}'\mu'}\,d^3r\right|^2=\sum_{i=0}^{2}\pi_i x^i\ , \tag{23}$$

where $\pi_0=a^4+\frac{1}{4}b^4-\sqrt{2}\,b^3c+2b^2c^2\ ,\qquad(24)$

$$\pi_1=2a^2(b^2+c^2)\ , \tag{25}$$

$$\pi_2=\tfrac{3}{4}b^4+\sqrt{2}\,b^3c+c^4\ , \tag{26}$$

and $a$, $b$, and $c$ are defined by Eqs. (10)–(12). With this result, one can evaluate the integral over the cosine of the scattering angle of Eq. (15) and determine $\Phi$. The result is

$$\Phi(k)=\sum_{i=0}^{2}\pi_i(\xi_k)\varphi_i(k)\ , \tag{27}$$

where

$$\varphi_0=-\frac{1}{(B^2-4AC)}\left(\frac{2(2A-B)}{A-B+C}+\frac{2A+B}{(B^2-4AC)^{1/2}}\ln R\right), \tag{28}$$

$$\varphi_1=\frac{1}{(B^2-4AC)}\left(\frac{2(B-2C)}{A-B+C}+\frac{(B+2C)}{(B^2-4AC)^{1/2}}\ln R\right), \tag{29}$$

$$\begin{aligned}\varphi_2=-\frac{2(A+B)}{A(B^2-4AC)}&\left(\frac{(B^2-2AC-2C^2)}{(A+B+C)(A-B+C)}+\frac{C}{(B^2-4AC)^{1/2}}\ln R\right)+\frac{BC}{A(B^2-4AC)}\\&\times\left(\frac{2(A-C)}{(A+B+C)(A-B+C)}+\frac{1}{(B^2-4AC)^{1/2}}\ln R\right)\\&-\frac{1}{2A^2}\left(\ln S-\frac{B}{(B^2-4AC)^{1/2}}\ln R\right)\ ,\end{aligned} \tag{30}$$

$$R=\left|(1-P)(1+Q)/(1+P)(1-Q)\right|\ , \tag{31}$$

$$P=[-B+(B^2-4AC)^{1/2}]/2A\ , \tag{32}$$

$$Q=[-B-(B^2-4AC)^{1/2}]/2A\ , \tag{33}$$

$$S=\left|(A+B+C)/(A-B+C)\right|. \tag{34}$$

The values of $\xi_F$ to be used in evaluating $\Phi$ and $\lambda$ are found by the solution of the secular equation[8]

$$\begin{aligned}\delta\xi^3+(1+\delta)\xi^2+\left(1-\frac{3\delta\hbar^2}{4\mu m_0E_g}k_F^2\right)&\\\times\,\xi-\frac{\hbar^2}{2\mu m_0E_g}k_F^2=0\ ,&\end{aligned} \tag{35}$$

with $k_F=(3\pi^2n_e)^{1/3}$. We note that $\xi_F$ is the largest root of this equation. The Hall mobility $\mu_H$ is then computed from the product $R_H\sigma$, where $R_H$ is the Hall constant.

## IV. RESULTS

Hinkley and Ewald[4] state that the donor impurities in the samples of Ref. 4 are probably antimony. No information is stated about the impurities in the samples of Ref. 5. One would expect the antimony donors to be singly charged, so we

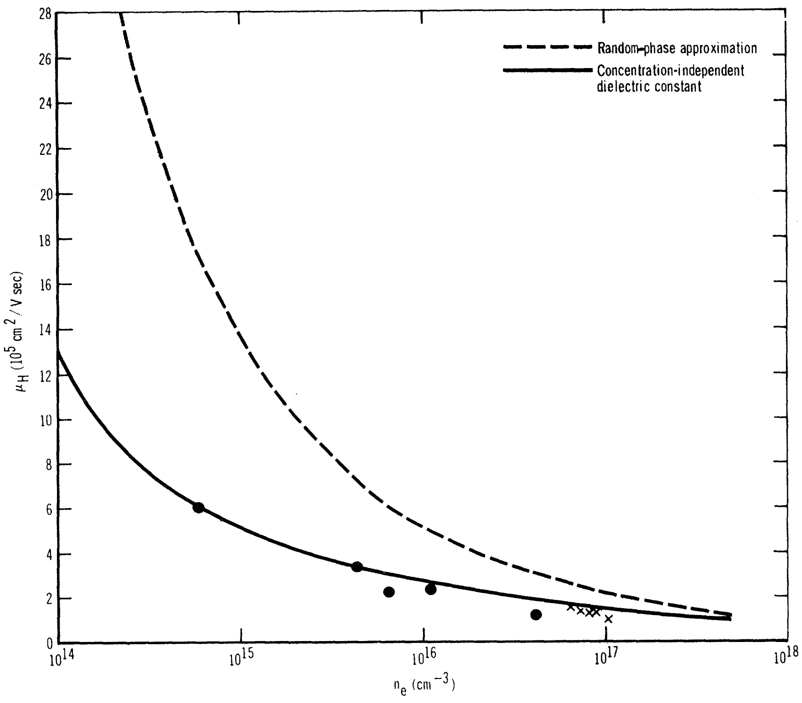

FIG. 2. Mobilities of degenerate $n$-type $\alpha$-Sn calculated for singly ionized donor impurities as a function of conduction-electron concentration. The solid curve is calculated using a concentration-independent dielectric constant and the dashed line a concentration-dependent dielectric function calculated in the random-phase approximation. The experimental points are from Ref. 4 (dots) and Ref. 5 (crosses).

will assume a $Z_i$ of 1. The results of this calculation are shown in Fig. 2. The mobilities calculated using the random-phase-approximation dielectric function are grossly larger than the experimental values[4,5] at low electron concentrations, where interband polarization is important, and larger than the experimental values at all concentrations. Also shown in this figure are the results of the calculation of Ref. 7 which used a concentration-independent background dielectric constant $\epsilon_0$, while still including the effects of $p$-like wave function and band nonparabolicity.[6] These results are in very good agreement with the experimental mobilities[4,5] over the range of concentration available.

Although it is difficult to imagine doubly charged antimony donors in $\alpha$-Sn, Fig. 3 shows the results of the random-phase-approximation mobility calculation for $Z_i = 2$. The agreement with experiment[4,5] is somewhat better than for $Z_i = 1$, but the results are still too high at low concentrations and are now too low at high concentrations. The concentration-independent dielectric constant curve is for $Z_i = 1$.

The large concentration dependence of the dielectric function in $\alpha$-Sn is a consequence, by way of the random-phase approximation, of the fact that the conduction-valence band degeneracy is symmetry induced. This peculiarity of the band structure is well established.[1,9] Thus, if the donor impurities in the available samples are singly ionized, then these results indicate that the random-phase approximation, as the principal physical approximation of the dielectric function calculation, considerably overestimates the interband polarization. Further experimental information on the charge states of the impurities and the mobility itself would be extremely important.

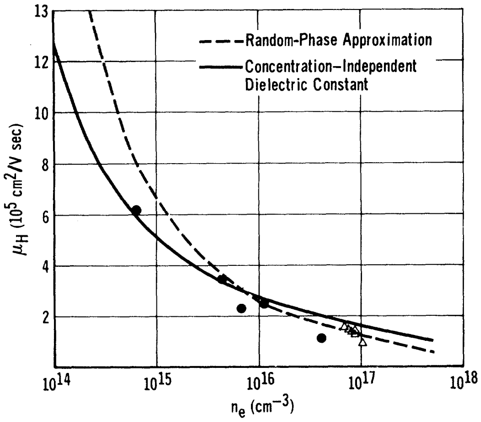

FIG. 3. Mobilities of degenerate $n$-type $\alpha$-Sn calculated for doubly ionized donor impurities in the random-phase approximation (dashed curve) and singly ionized donor impurities using a concentration-independent dielectric constant (solid curve). Experimental points are from Ref. 4 (dots) and Ref. 5 (triangles).

## ACKNOWLEDGMENTS

I would like to thank Dr. C. R. Whitsett, Dr. S. L. Lehoczky, and Dr. D. P. Ames for several discussions of this problem. I would like to thank Dr. D. P. Ames and Dr. J. E. Dueker for support of this work.

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[*] Research conducted under the McDonnell Douglas Independent Research and Development Program.

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