Condensed Phase of Lithium Impurities in Silicon

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We have calculated the ground-state energy as a function of density for a recently suggested condensed phase of lithium impurities in silicon. The temperature-density phase diagram of this system has been determined and it is found that the critical temperature and density are 3.0×10^2 °K and 3.5×10^{19} cm^{-3}, respectively.

In this Letter we present a calculation of the ground-state energy and thermodynamic properties of a possible condensed phase of Li impurities in Si. The existence of such a phase has recently been suggested by a number of experimental results. Kastalskii and Maltsev[1] observed the solid-state precipitation kinetics for a supersaturated solution of Li in Si by means of electrical-conductivity and Hall-effect measurements. Subsequently, Vengalis, Kastalskii, and Maltsev[2] measured the infrared reflectance of a heavily doped Si:Li system. Both experiments yielded anomalous data which could be explained by assuming that the Li impurities undergo a gas-liquid phase separation at room temperature for impurity densities between 10^{19} and 10^{20} cm^{-3}.

Li goes into Si interstitially as a shallow donor. The low-lying excitations of the donor electron are well understood in terms of the effective-mass approximation,[3,4] For a uniform distribution of Li impurities in Si having a density greater than approximately (2 or 3)$\times10^{18}$ cm^{-3}, the system will be metallic, and the calculation of the zero-temperature ground-state energy is then analagous to a cohesive energy calculation for a normal metal. This ground-state energy will have its minimum at a fairly high density, $n_{\text{min}} \approx 10^{20}$ cm^{-3}. If the Li impurities were mobile at zero temperature, and introduced uniformly at a density less than n_{min}, then the system would become inhomogeneous with all of the Li in a condensate of density n_{min}. For a range of temperatures above absolute zero, the condensate can coexist with a low-density "vapor" phase. Above a critical temperature T_c only one phase exists, and the system becomes homogeneous.

As stated by Kastalskii and Maltsev, the observation of the condensed phase depends on the following considerations. The mobility of Li in Si decreases exponentially with decreasing temperature.[5] Below a certain temperature which we denote by T_f, the Li becomes essentially immobile. For the condensed phase to be easily observable, it is necessary that the phase transition occur for a range of temperatures above T_f. So a major question arises as to whether the critical temperature T_c of the condensed phase is greater than or less than the freezing temperature T_f. The purpose of this Letter, then, is to investigate the thermodynamics of this system, and to establish a value for the critical temperature.

The initial step in calculating T_c is to evaluate the zero-temperature ground-state energy of the condensate as a function of density. This was done using the Kohn-Sham formulation of the density-functional formalism.[6] Since the electronic energy of the system is not expected to depend sensitively on the arrangement of the Li impurities, it is convenient to imagine them as being distributed on a periodic lattice. The electrons are treated, within the effective-mass approximation, as moving in an effective periodic potential consisting of the total electrostatic potential plus the exchange-correlation potential. The single-particle states for this problem are then obtained approximately by requiring them to satisfy the Bloch condition on the surface of a spherical Wigner-Seitz cell. A variational approach due to Kohn[7] is used to obtain a secular equation determining the energy for a given wave vector, $\vec{k}$. The density, generated from the wave functions for energies between the bottom of the band and the Fermi energy, is used to define a new effective potential, and the procedure is repeated to self-consistency. The method described above was first used by Tong[8] in a calculation of the cohesive energy of sodium.

In performing the calculations, it was convenient to use the following units: The unit mass is the density-of-states mass ($m_{\rm dens}$) of the electrons (0.32 times the free-electron mass); the unit of energy, 1 Ry* $= m_{\rm dens}e^4/(2\hbar^2\kappa^2) = 33.7$ meV; and the unit of distance, $a_b^* = \hbar^2\kappa/(m_{\rm dens}e^2) = 18.9$ Å. Here $\kappa = 11.4$ is the static dielectric constant of Si.

The energy functional we used consisted of the kinetic energy $T_s[n]$, the direct electrostatic energy $E_{es}[n]$, and a local approximation for the exchange and correlation energy $E_{xc}[n]$.

The kinetic energy term is approximated by replacing the six ellipsoidal conduction bands with six spherical bands with the density-of-states mass. The value of the exchange energy as a function of density has been given by Combescot and Nozières[9] as $\epsilon_x = -0.478/r_s$ Ry*. Finally, the correlation energy for the uniform electron gas in Si was calculated within the random-phase approximation, including both the conduction-band anisotropy and degeneracy (Fig. 1).

The calculated ground-state energy as a function of density is plotted as curve *c* in Fig. 2. The minimum of the energy-density curve yields an equilibrium bulk density of 2.1×10^{20} cm^{-3} at zero temperature, and a ground-state energy per electron-ion pair of -2.55 Ry*. This corresponds to a binding energy of approximately 1.5 Ry* relative to the isolated donor. This binding energy per electron-ion pair is surprisingly large, being a factor of 4 larger than the binding energy per pair for the electron-hole liquid (EHL) in Si. In order to illustrate the origin of the large binding energy, we plot three curves in Fig. 2 for the zero-temperature ground-state energy, $\epsilon(r_s)$. Curve *a* shows $\epsilon(r_s)$ within the Hartree-Fock approximation (HFA), assuming a uniform electronic density within a spherical Wigner-Seitz cell. For curve *b*, we include the RPA electron correlation energy for the uniform density model. Our final result is given by curve *c*, in which we allow the electron density to relax around the Li$^+$ cores, and includes the electrostatic interactions and exchange-correlation effects self-consistently within the density-functional formalism. As can be seen, the Si:Li condensate is already strongly bound (with respect to isolated impurities) within the HFA. The origin of the binding of the condensate lies in the very strong electrostatic interaction between the Li$^+$ cores and the electrons. For example, within the HFA the direct electrostatic energy contributes 4 times as much to the binding as does the exchange energy. In the EHL, on the other hand, both the electrons and holes are delocalized and there is no direct electrostatic contribution to the bulk energy. Curve *b* shows the importance of correctly including the correlation energy for the electrons which increases the

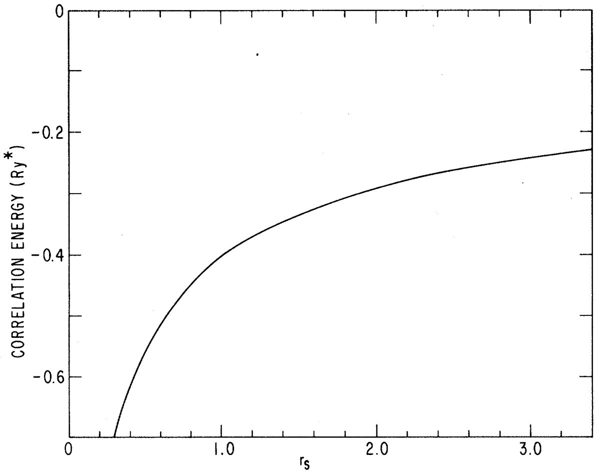

FIG. 1. Correlation energy per particle for electrons in Si conduction bands, as a function of r_s. 1 Ry* = 33.7 meV.

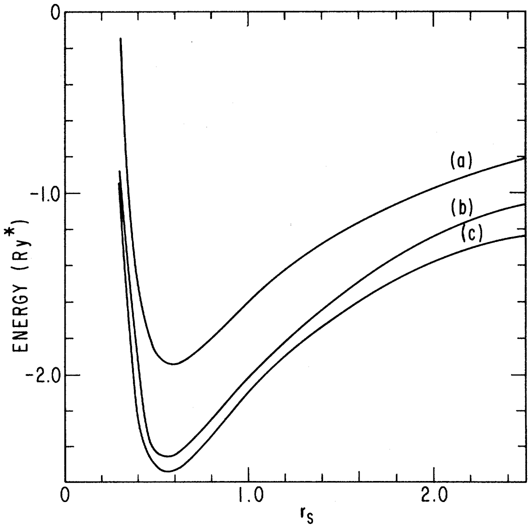

FIG. 2. Ground-state energy per electron-ion pair in various approximations: *a*, Hartree-Fock with uniform electron density; *b*, Hartree-Fock plus correlation energy with uniform electron density; *c*, self-consistent calculation.

binding energy of the condensate by 40%. Finally, curve *c* shows that the relaxation of the electrons to the ion cores increases the binding energy by a relatively small amount, i.e., 5%.

In using the results for $\epsilon(r_s)$ to calculate the thermodynamic properties of the Si:Li system, we note that the present calculation gives a more reasonable result in the low-density limit than the equivalent calculation for the electron-hole liquid since ϵ approaches a value of about -1 Ry* as $r_s \to \infty$, corresponding to an isolated bound donor. On the other hand, current calculations for the bulk EHL conclude that $\epsilon(r_s)$ tends to zero for large r_s rather than the correct limit of -1 Ry* for an isolated exciton. It is therefore reasonable to attempt a calculation of the phase diagram of this system for all densities above the Mott transition. The calculation is analogous to the "plasma model" used for the EHL, as first discussed by Combescot.[10] The free energy per electron, f, and the chemical potential μ are calculated as a function of temperature T and r_s. For $T=0$, we have $f=\epsilon$ and $\mu=\partial(n\epsilon)/\partial n$, where n is the density: $n^{-1}=4\pi r_s^{\,3}/3$. For finite T, the changes in f and μ are calculated for a model of noninteracting fermions assuming that only the kinetic energy changes with temperature. Since the calculation is done for values of T on the order of the Fermi energy, we cannot use low-temperature expansions for Δf and $\Delta\mu$, but must calculate these quantities numerically.

Once $\mu(T)$ and $f(T)$ are known, the pressure is obtained using $P=n(\mu-f)$. The phase diagram is constructed by fixing T and searching for two different values of r_s for which the pressures and the chemical potentials are equal. This phase separation occurs below a temperature, T_c, calculated to be 301°K as shown in Fig. 3. For T below 200°K, the calculated density of the vapor phase is very small; in this region, the density of the condensed phase is determined from the condition that $P=0$. The exact behavior of the low-density phase for low temperature is not predicted by the present calculation. In the region of densities below about 2×10^{18} cm^{-3}, the vapor pressure depends on the existence of Li complexes, etc., which are not considered in our calculation of $\epsilon(r_s)$.

Our calculated value of T_c is indeed above the freezing temperature $T_f \simeq 240$°K reported by Kastalskii and Maltsev.[1] However, the experimental results of Refs. 1 and 2 seem to indicate that the critical temperature of the condensate lies between 300 and 400°K, which is somewhat higher than our approximate value of 3.0×10^2°K. We therefore mention some of our approximations which could account for the difference. The entire calculation was carried out within the effective-mass approximation, which is known to be quite good for isolated Li impurities in Si. However, the density in the Li$^+$ core region is greater for the condensate than for the isolated impurity. Hence, it is possible that central-cell corrections may play some role in determining the value of T_c. Central-cell corrections, typically, will make $\epsilon(r_s)$ more negative,[4] and will tend to increase the calculated critical temperature.

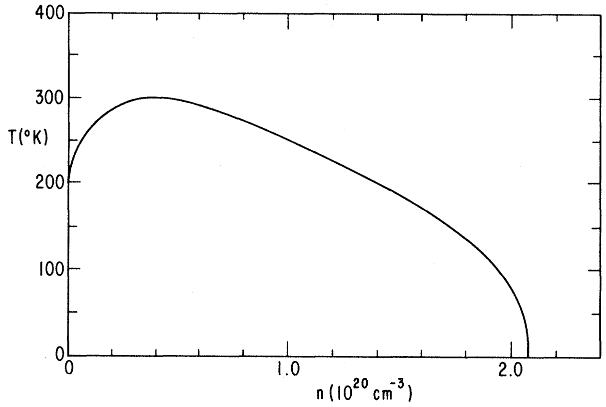

FIG. 3. Temperature-density phase diagram for the lithium condensate in silicon.

Another approximation in the calculation of the critical temperature was the assumption that the temperature dependence of the free energy was due only to that of the electronic kinetic energy. As noted by Thomas, Rice, and Hensel,[11] the temperature dependence of the exchange and correlation contribution to the free energy, f_{xc}, is not important for temperatures significantly below the plasma frequency, as is true for our T_c. Furthermore, in the Si:Li problem f_{xc} is typically $\frac{1}{2}$ of the direct Coulomb interaction. Thus the temperature dependence of f_{xc} is even less significant for the determination of T_c in this case than for the corresponding EHL problem. Also ignored were possible many-body effects, such as electron-phonon and electron-electron interactions, on the band mass. The various approximations discussed above may change the critical temperature and density of the condensate somewhat, but are not expected to change the qualitative nature of the phase diagram.

The major characteristic of the Si:Li system is a phase separation which occurs at room temperature. Although current experimental results can be explained in terms of this model, the experimental data are not sufficient to characterize adequately the fundamental properties of the system. For example, the densities of the two phases as functions of temperature are as yet undetermined, as are the critical temperature and density. One experimental difficulty in observing this phase separation is the fact that at the temperatures and Li densities of interest, the Li ions are present at supersaturated concentrations.[12] Consequently, the Li ions tend to precipitate out of the Si at the surface and at defects in the bulk. However, the precipitation phenomenon takes place much more slowly than does the expected phase separation, so that although the two-phase system described here is only metastable, this fact should not prevent its observation and characterization.

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Theory of the Temperature Dependence of the Electric Field Gradient in Noncubic Metals*

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The temperature dependence of the electric field gradient $eq(T)$ in noncubic metals is calculated within a pseudopotential approach including the influence of lattice vibrations. The resulting $eq(T)$ factorizes into a Debye-Waller factor and a lattice sum over screened ions. The accurately measured $eq(T)/eq(0)$ values for In, Cd, Zn, Sb, and Sn are quantitatively reproduced using known data for the lattice constants and for the mean-square atomic displacements.

Since the pioneering work of Simmons and Slichter[1] on In metal many more experiments have been performed by nuclear quadupole resonance (NQR) and perturbed angular correlation methods to determine accurately the temperature dependence of the electric field gradient (EFG) $eq(T)$ at a nuclear site in noncubic metals. Recently, Heubes *et al.*[2] discovered in a heuristic way that the $eq(T)$ data in all nontransition metals can be well reproduced by a $T^{1.5}$ dependence. Attempts to explain this temperature dependence have been far from successful. Within the traditionally used *Ansatz*[3] $eq = (1-\gamma_\infty)eq_{\text{ion}} + (1-R)eq_{\text{el}}$ one calculates the point-charge interaction of the ion cores eq_{ion} by a Coulomb potential and separately adds the interaction with the conduction electrons, q_{el}, which has been evaluated by complicated band-structure calculations. The temperature dependence of eq_{ion} due to the variation of lattice parameters is much too small (and in most metals even wrong in sign) to explain the observed $eq(T)$ data.

Simmons and Slichter[1] and Quitmann, Nishiyama, and Riegel[4] considered within rough approaches thermal lattice vibrations as a further possible contribution to $eq(T)$, but in Ref. 1 this contribution has been calculated to be negligible, whereas in Ref. 4 the strength parameter of this contribution was treated as a fitting parameter to the experimental $eq(T)$ data in In.

In this paper we present a theory by which the experimentally observed temperature dependence of $eq(T)$, e.g., in Zn, Cd, In, Sn, and Sb, can be explained quantitatively. Unambiguously the temperature dependence of $eq(T)$ arises from the temperature dependence of the lattice constants