

Even in a perfect, stationary lattice it seems likely that this change may sometimes cause the use of a less favorable orbital and a finite increase in energy. But in a distorted lattice the new state clearly requires the use of a less favorable orbital, because, in order to maintain uniform charge distribution, the additional orbital must be selected within a very limited region of space. Thus we conclude that unpairing two electron spins will cause a finite increase in energy in a vibrating lattice.

The writer does not claim to have proved rigorously this essential point, but he does believe that the best available theoretical arguments strongly indicate the correctness of this finite excitation energy. Also, he is aware of no disproof.

While we shall not discuss the transition to the normal state in any detail, it seems safe to assume that the transition temperature is of the order of magnitude  $\epsilon/k$ , where  $\epsilon$  is the energy required to unpair the first spin. We shall give some explicit support for this relationship later. For a rigid perfect lattice we believe that this energy may still have a nonzero value  $\epsilon_\infty$  in at least some substances. In all cases, however, we expect the electronic energy to rise quadratically with lattice distortion and to rise slightly more steeply when a spin is unpaired. Thus we expect a term  $\epsilon(M)$  proportional to the square of the amplitude of the lattice vibrations or to  $M^{-1/2}$  if  $M$  is the atomic mass.

Thus we have

$$kT_c \cong \epsilon = \epsilon_\infty + \epsilon(M) = \epsilon_\infty + (\text{const.}) M^{-1/2}. \quad (2)$$

If  $\epsilon_\infty$  is negligible, one expects  $T_c$  to vary with  $M^{-1/2}$ , as was observed for mercury.<sup>6</sup> In the case of tin<sup>7</sup> the reported exponent of  $M$  is  $-0.462 \pm 0.014$ , which deviates from  $1/2$  by about three times the stated error. This offers some indication that  $\epsilon_\infty$  may be significant for tin.

Thus the isotope effect is satisfactorily explained in this theory. It is also interesting to note that these energy terms are very small in comparison with the total zero-point energy of lattice vibration. Consequently no large difference in lattice constant, elastic constants, or lattice specific heat is expected between normal and superconductive states.

## II

Next let us consider the possibilities of low-energy thermal excitation of the completely paired electronic system. Pines and Bohm<sup>8</sup> have shown that density oscillations of the usual phonon type have a very high energy in fluid of electrically charged particles and that they will not be excited in the electronic system of metals at low temperatures. The phonons in a metal are to be regarded as lattice motions. The accompanying electronic adjustment for lattice phonon motion is exactly similar to that for lattice zero-point oscillations. The electronic system is still in its ground state.

We have already mentioned the possibility of translational motion of the entire electronic system with respect to the lattice. This requires, of course, that the superconductor be appropriately connected for current flow. There is also the possibility of nonuniform flow, provided the flow rate varies only slowly.

Since all density oscillations are of high frequency and high energy, we may conclude that, as long as all electrons are paired, the only low-energy motion is the translational flow just mentioned. This is such an important point, however, that we shall attempt to show more explicitly the absence of other low-energy states.



By complete electron pairing we mean, of course, that there are equal numbers of electrons with positive and with negative spin. Moreover, we expect that the wave function will be large only for electron locations which constitute an essentially uniform distribution of electrons of each spin as well as uniform distribution of total electronic charge.

Now let us suppose that an electron of positive spin moves slowly from a region A to another region B. In order to maintain uniform charge density (in the absence of net flow), another electron must be transferred from B to A. If the second electron also has positive spin, we do not have an experimentally distinguishable state. We have merely the exchange of two electrons, which leaves the wave function unchanged except for a reversal of sign. This is just the property of the ground state; we have no new state.

The other possibility is that the charge compensation occurs through the motion from B to A of an electron of negative spin. Now we have in region B an excess of two positive spins and in region A an excess of two negative spins. Provided that regions A and B are sufficiently far apart, this is clearly a new state. Its wave function can be orthogonal to that of the ground state. But its energy will exceed that of the normal state by approximately twice the energy of spin unpairing together with any excess electronic kinetic energy. Consequently it is not a low-energy state in the sense of having lower energy than that required to unpair spins.

It is difficult to predict whether there will be states of the type just described where the energy is not sufficient to "dissociate" the regions A and B of excess positive and negative spin. However, detailed consideration indicates that the energies of such states almost certainly must exceed that of a state with a single pair of electrons of parallel spin. Consequently this question is of secondary importance.

We now conclude that in the first approximation the low-energy excited electronic states (other than those for current flow) may be described in terms of unpaired electron spins. If the spin of one electron is reversed, then in the region immediately around it there will be an excess of two electrons of a given spin. These two electrons may then separate to form two regions with single excess spin. Each region may move through the lattice. Thus the location and motion of each region of excess spin comprise observable features which can characterize a large array of excited states.

The momentum associated with such excitations can interact with the lattice phonons of appropriate wave length. Thus the electronic specific heat of the superconductor will be in thermal equilibrium with the lattice. On the other hand, there does not appear to be any mechanism whereby lattice oscillations can directly create such electron-spin excitations. They must be created at a surface or an interior defect or may be transferred into a superconductive region from a nonsuperconductive region of the metal. This picture is in accord, in general features at least, with the observed facts on the kinetics of the phase transition in superconductivity.<sup>9</sup>

The superconductive properties arise because the infinitesimal energy quanta of translation of the entire electronic system are unable to excite either phonons or electron excitations of the spin-unpairing type. For electronic motion to excite phonons the force exerted on the lattice atoms must vary from atom to atom with