This work has been supported financially by the Swedish Atomic Energy Committee. The ready assistance of Mr. B. Nagel and Mr. S. G. Nilsson is gratefully acknowledged.

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 The values of a and a, given in Table II are much more accurate, being closely connected with the eigenphases, which are stationary in the varia-tional method used. See L. Hulthén, Kgl. Fysiograf. Sällsk. Lund För-handlingar 14, No. 21 (1944); Arkiv f. Mat. Astr. o. Fys. 354, No. 25 (1948). Smith, Barkas, Bishop, Bradner, and Gardner, Phys. Rev. 78, 86 (1950).
 In addition to Eq. (2) we have the well-known relation

 $\sigma_0 = 3\pi a_{l^2} + \pi a_{s^2}$

⁷ L. Hulthén and S. Skavlem (unpublished manuscript, 1949).

The Hyperfine Structure of Ni⁶¹

KARL G. KESSLER National Bureau of Standards, Washington, D. C. May 5, 1950

NTERFERENCE spectrograms of nickel¹ enriched to 80 percent in Ni⁶¹ have been made with a liquid-nitrogen-cooled beryllium hollow cathode discharge tube filled with helium and argon. Fabry-Perot interferometers having 15, 25, 50, and 67 mm Invar separators were used with aluminum-coated quartz plates. No clear hyperfine structure splitting has been observed, but certain lines in the spectrum, especially those involving the $d^{9}s^{3}D_{3}$ level, show definite broadening in excess of that caused by the Doppler effect.

The lines involving transitions to the ${}^{3}D_{3}$ level, in the region 3300 to 3600A, show a half-width of approximately 0.06 cm^{-1} . This is very nearly double the half-width of the sharpest lines from other transitions in the same region. The approximate halfwidth of these sharpest lines, 0.03 cm⁻¹, is very nearly equal to the limit of 0.025 cm⁻¹ determined by Doppler broadening at liquid nitrogen temperatures. The resolution was insufficient to determine the spin, but the upper limit of the magnetic moment appears to be of the order of 0.25 nuclear magneton. Further study of this isotope by using liquid hydrogen cooling is contemplated.

¹ Produced by the Y-12 plant, Carbide and Carbon Chemicals Corpora-on, Oak Ridge, Tennessee, and obtained by allocation from the United States AEC.

On the Origin of the Sodium D Lines during Twilight

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PENNDORF¹ has recently proposed a new mechanism to explain the twilight luminescence of atmospheric sodium. This was done mainly in order to account for certain experimental results, found by Vegard and Kvifte,² which are hard to interpret on the usual theory. Unfortunately the new process itself raises great difficulties.

According to Bricard and Kastler³ the intensity of the D line emission at twilight is about 1.5×1010 photons/cm² column/sec., or 10⁴ photons/cm³/sec. in a 15 km layer. To account for this Penndorf has suggested the following series of reactions, supposed to take place near 100 km height:

$$Na+N_2O=NaO+N_2,$$
 (1)

$$NaO + Na_2 = Na(^2P) + Na_2O, \qquad (2)$$

$$Na(^{2}P) = Na(^{2}S) + h\nu(\lambda = 5890A),$$
 (3)

$$\mathrm{Na}_{2}\mathrm{O}+h\nu=\mathrm{Na}_{2}+\mathrm{O}.$$
(4)

The rate of (2) must be α [NaO][Na₂] = 10⁴ reactions/cm³/sec., in order to give the observed intensity of emission. The value of α is probably 10-10 cm3/sec.

The four reactions quoted are to be considered together with (5) and (6):

$$Na_2 + h\nu = Na + Na, \qquad (5)$$

$$Na+Na+X=Na_2+X.$$
 (6)

Equation (5) denotes the photo-dissociations of Na₂ by light of wave-length $\lambda = 3500 \text{A} - \lambda = 2900 \text{A}$. The rate of this reaction is δ [Na₂]; here $\delta = (\pi e^2 \lambda^2 / mc^2) fI$, where f is the oscillator strength of the transitions leading to the dissociation, and $I(\sim 4 \times 10^{20}$ photons/cm/cm²/sec.) stands for the intensity of solar radiation in the spectral region concerned. Thus $\delta \sim 3.6 \times 10^{-1} f$; even with f as small as 10^{-3} , $\delta > 10^{-4}$.

Three-body recombination (6) of Na atoms seems to be faster than radiative association; with a local particle density $[X] = 10^{14}$ its rate would be about 10⁻¹⁶[Na]². For equilibrium between (5) and (6)

or

$$\delta[Na_2] = 10^{-16}[Na]^2$$

$$[Na_2] \leq 10^{-12} [Na]^2$$

and by the conditions for reaction (2)

$$[NaO] \ge 10^4/\alpha \cdot 10^{-12} \cdot [Na]^2 = 10^{26}/[Na]^2.$$

Table I lists some possible values of [Na] and corresponding minimum values of [NaO].

TABLE I. Possible values of [Na], and corresponding minimum values of [NaO].

[Na]	[NaO] min	
104	1018	
105	1016	
106	1015	
2×10 ⁶	2.5×1013	

By consideration of the Na+: Na equilibrium in an ionized region it has been shown by the writer⁴ that the greatest possible value of [Na] is 2×10^6 atoms/cm³ at the heights concerned. Thus, in order to make Penndorf's process work, the concentration of NaO must be impossibly high (at least 25 percent).

Some of the values adopted in the calculation may be rather unfavorable to the new process, but it is clear that the ratio [NaO]: [Na] will always be very large. This again would be hard to explain, as NaO is probably dissociated not only by reaction (2), but also by sunlight, and by its reaction with atomic oxygen

$$NaO+O=Na+O_2$$
.

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Zero-Point Vibrations and Superconductivity

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Bell Telephone Laboratories, Murray Hill, New Jersey May 22, 1950

.THEORY of superconductivity which depends on inter-A action of the valence electrons with the zero-point vibrations of the crystal lattice is proposed. This approach was stimulated by the recent finding of Reynolds, Serin, Wright, and Nesbitt¹ and of E. Maxwell² that the critical temperature, T_c , of mercury depends on the isotopic mass. The theory is a modification of one proposed some years ago by the writer.³ It gives a natural explanation of the isotope effect and the energies and critical temperatures are of the correct order.

It is assumed that the vibrational modes of the superconducting state differ from those of the normal state in that the vibrations are such as to lower the energy of electrons in states near the surface of Fermi distribution, $E = E_0$. The normal modes in the superconducting state are assumed to consist in part of wave groups which extend over distances of the order of 10⁻⁶ cm and which have average wave vectors which connect electron states with energies near E_0 . This implies a correlation between the displacements of ions from their equilibrium positions which extends over distances of this order. It will be shown below that it is reasonable to expect that coherence over distances of $\sim 10^{-6}$ cm will give a lower energy for the electrons than coherence over larger or smaller distances. Interaction with these modes gives rise to new states which are linear combinations of the ψ_k with E near E_0 and which have energies which differ from the old by $\sim \Delta E$. If the interactions are such as to depress the levels just below E_0 and raise those just above, there will be a net decrease in electron energy if $kT \sim \Delta E$ or less. We therefore assume that $kT_c \sim \Delta E$. The normal modes of the superconducting state have a lower zero-point energy than those of the normal state.

It is presumed that the motion of the electrons is sufficiently rapid so that the wave functions are those appropriate to a fixed position of the ions at any moment and that they follow the motion of the ions adiabatically.4

Superconductivity follows as in the earlier theory.⁵ Electrons in the superconducting states near the Fermi surface have a small effective mass. These states are linear combinations of ψ_k with small net current, but which are easily modified by an external field to give a large current. That superconductivity follows from the model is also suggested by Slater's theory.6 The wave functions of the electrons in the superconducting state extend over the region of coherence of the lattice vibrations. Slater showed that wave functions extending over \sim 137 atom diameters may be expected to give a large diamagnetism and lead to superconductivity.

To get a rough estimate of the nature of the normal modes and of the interaction energies involved, we consider a volume V which contains only a small number p of states with energies within $\Delta E \sim kT_c$ of E_0 . The usual normal modes for a volume of this size will presumably be similar to the normal modes of the superconducting state. It is necessary to take the volume small because the amplitude of the zero-point motion varies as V^{-1} , but if the volume is taken too small one cannot confine the wave functions of the electrons to the region of coherence without an increase of Fermi energy. If $N(E)\Delta E$ is the number of states/cm³ in ΔE , we take

$$V \sim p / [N(E)\Delta E]. \tag{1}$$

The energy changes, ΔE , resulting from the interactions are of the order of the matrix element

$$\Delta E \sim |M_{kk'}|_{Av} = |\int_V \psi_{k'}^* U \psi_k d_\tau|_{Av}, \qquad (2)$$

where U, the interaction potential for a mode which connects k and k', is proportional to the displacement of the ions. We can estimate the magnitude from conductivity theory. For a mode with zero-point energy $\frac{1}{2}h\nu = \frac{1}{2}\kappa\Theta$ in the volume V:

$$|M_{kk'}|_{AV^2} = (\Theta/2TV)(e^2/3\pi\hbar)[dE/dk]^2\rho.$$
(3)

The resistivity ρ is taken at a high temperature such that ρ/T is a constant.⁷ Using (1) for V, and setting $|M_{kk'}|_{AV} = \Delta E$, we find from (3) that

$$\kappa T_c \sim \Delta E \sim (\Theta N(E)/2T\rho) (e^2/3\pi\hbar) [dE/dk]_m^2 \rho.$$
(4)

A high density of electrons in a wide energy band and a large interaction between electrons and lattice are favorable for superconductivity. The theory gives T_e proportional to Θ , as observed empirically by Serin, Reynolds, and Nesbitt⁸ in Hg isotopes.

An estimate of T_c can be obtained by expressing N(E) and dE/dk in terms of the concentration of valence electrons, n_{ϵ} , in the free electron approximations. The result is:

$$T_{c} \sim (\hbar e^{2}/4\pi m) (\Theta_{\rho} n_{e}/\kappa T_{\rho}) \sim 1.5 \times 10^{-4} (n_{e} \Theta_{\rho}/T_{\rho}).$$
(5)

This gives the right order of magnitude for T_c for the "soft" superconductors if we take $p \sim 10$ to 20, which is a reasonable value. The volume V is then $\sim 10^{-18}$ cm³ for $n_e \sim 10^{23}$ /cm³.

The decrease in electron energy per unit volume at T=0 is of the order

$$W_{e} \sim N(E) \Delta E \times \Delta E = N(E) (\Delta E)^{2} \sim 3n_{e} (\Delta E)^{2} / 2E_{0}.$$
⁽⁶⁾

For $n_e \sim 10^{23}$ /cm³, $\Delta E \sim 5 \times 10^{-16}$ erg, $E_0 \sim 5 \times 10^{-12}$ erg, Eq. (6) gives $W_c \sim 7.5 \times 10^3$ which corresponds to $H_c \sim 400$ oersteds. The theory predicts that H_c at T=0 should vary in the same way with isotopic mass as T_c .

The writer is indebted to Dr. B. Serin for communicating the data of the Rutgers group in advance of publication and to Dr. C. Herring for a critical reading of the manuscript.

¹ Reynolds, Serin, Wright, and Nesbitt, Phys. Rev. 78, 487 (1950).
² E. Maxwell, Phys. Rev. 78, 477 (1950).
³ J. Bardeen, Phys. Rev. 78, 477 (1950).
³ J. Bardeen, Phys. Rev. 79, 928(A) (1941). Zero-point displacements replace the small periodic distortion of the former theory.
⁴ The time taken for an electron with a velocity ~10³ cm/sec. to go ~10⁻⁶ cm is ~10⁻¹⁴ sec.; about one-tenth of usual vibrational periods.
⁶ Peierls' modification of the Landau theory gives a large diamagnetism for electrons of very small effective mass. It will be shown in a subsequent publication that such a model leads to a theory of superconductivity of the London type.
⁶ J. C. Slater, Phys. Rev. 51, 195 (1937); 52, 214 (1937).
⁷ For the theory on which (4) is based, see, for example, N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Oxford University Press, New York), Chapter VII.
⁸ Serin, Reynolds, and Nesbitt, Phys. Rev. 78, 813 (1950).

On the Production of Penetrating Showers in Lead and Carbon

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N experiment has been performed at the Laboratorio della Testa Grigia, Cervinia (3500 m) to study the dependence of the mean free path for production of penetrating showers (p.s.) on the atomic number of the generating layer, and the total number of ionizing particles in the shower. The counter arrangement is sketched in Fig. 1. The counter telescope ABC (active



surface of each counter 4×10 cm², distance between the axes of counters A and C = 32 cm) defined the solid angle of the incident radiation. The counters of the trays S, H, E, E', were connected to four addition circuits; in the set S counters indicated with the same number were connected in parallel; in the set H the counters were separated from each other by a thickness of about 1 cm Pb, and from the counters S by an absorber $\gamma = 7.5$ cm Pb; the 14 counters L, which surrounded the telescope ABC on all sides, were all connected in parallel. Two lead absorbers α and α' , 1 cm