Calculation of the Superconducting Transition Temperature

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(Received 15 June 1967)

An explicit expression is derived for the superconducting transition temperature in an isotropic superconductor. The calculation includes three improvements over previous work. Firstly, strong-coupling effects are included; secondly, both normal and umklapp contributions are evaluated in detail in calculating the electron-phonon interaction; and thirdly, a more realistic approximation to the lattice is obtained by including a Coulomb pseudopotential and correcting the jellium ionic plasma frequency with the use of the measured sound velocity. The theory is applied to the case of the lanthanum selenide system, in which one can vary the electron concentration independently of other material parameters and measure the superconducting transition temperature as a function of this variation. The theory accounts very well for the observed transition temperatures over the whole measured range from 1 to 10°K.

INTRODUCTION

THERE have been a few moderately successful attempts in the past at the quantitative determination of the superconducting transition temperature (T_c) in metals.[1-4] These calculations, however, have been more of an order of magnitude or, at best, a factor of 2–3 estimate rather than a precise quantitative calculation. The main reason for this is that the detailed knowledge of the electronic and lattice properties necessary for a good calculation is available only for the elements, which means that one must perform a calculation yielding a single number (i.e., T_c of the element in question). Since there are, in general, unknown or not reliably known constants in any many-body calculation, a single number is not a good check on the theory. What one really needs is a system where one parameter of interest may be varied independently of the others (or at least relatively so) in order to study the functional dependence of T_c. The alloy systems in which this can be done are usually quite complicated and the present theory has not been adequate for calculating these.

The discovery that the lanthanum selenide system[5-7] has particularly simple electronic properties and a high T_c has given us a material which is simple enough to calculate the properties of interest but allows extensive and quantitative comparison between theory and experiment. The description of this system and its various desirable properties are described in the following paper.[8] In the present paper, with the goal of a good experimental test in mind, I will proceed to describe a calculation which allows a close comparison with the functional behavior of T_c.

CALCULATION OF T_c

The starting point for the calculation is the work of Morel and Anderson,[3] in which the Eliashberg gap equation is solved, including both the electron-phonon attractive coupling and the Coulomb repulsion. They then calculated the electron-phonon and Coulomb repulsion coupling parameters using a jellium model of a metal. The results obtained for T_c from this calculation are of the right order of magnitude but do not exhibit real quantitative agreement with experiment.

There are three improvements that must be made in the calculation. Firstly, strong-coupling corrections must be included. In fact, for the calculation of T_c, these corrections are not negligible for materials with $T_c > 0.5°K$. Secondly, Morel and Anderson calculated the electron-phonon coupling constant λ for monovalent metals by considering only normal processes, and for polyvalent metals by considering only umklapp processes over one zone. These assumptions greatly underestimate the proper contribution and, in fact, predict $\lambda \leq \frac{1}{2}$. The present calculation will consider each zone in the reciprocal lattice separately and calculate the contribution of each zone over the part of the Fermi sphere appropriate to that zone. Thirdly, corrections to the jellium approximation will be made by replacing the Coulomb potential with a pseudopotential containing a core-repulsion term and by replacing the plasma frequency by the Debye frequency in the jellium phonon spectrum.

The inclusion of the strong-coupling corrections has

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[1] David Pines, Phys. Rev. 109, 280 (1958).
[2] J. M. Ziman, Phys. Rev. Letters 8, 272 (1962).
[3] P. Morel and P. W. Anderson, Phys. Rev. 125, 1263 (1962); Pierre Morel, J. Phys. Chem. Solids 10, 277 (1959).
[4] J. C. Swihart, D. J. Scalapino, and Y. Wada, Phys. Rev. Letters 14, 106 (1965); and *Low Temperature Physics* (Plenum Press Inc., New York, 1965), Vol. 9, Part A, p. 607; D. J. Scalapino, Y. Wada, and J. C. Swihart, Phys. Rev. Letters 14, 102 (1965).
[5] R. M. Bozorth, F. Holtzberg, and S. Methfessel, Phys. Rev. Letters 14, 952 (1965).
[6] G. L. Guthrie and R. L. Palmer, Phys. Rev. 141, 346 (1966).
[7] P. E. Seiden and F. Holtzberg, in *Proceedings of the Tenth International Conference on Low-Temperature Physics, Moscow, 1966* (Proizvodstrenno–Izdatel'skii Kombinat, VINITI, Moscow, USSR, 1967).

[8] F. Holtzberg, P. E. Seiden, and S. von Molnar, following paper, Phys. Rev. 168, 408 (1968).

recently been simplified by the work of McMillan.[9] He has obtained a new solution of the gap equation which gives the relation for T_c as

$$T_c = \Theta_D \exp\left[-\frac{(1+\lambda)}{(\lambda-\mu^*-(\bar{\omega}/\omega_D)\lambda\mu^*)}\right], \quad (1)$$

where Θ_D is the Debye temperature, μ^* is the Coulomb repulsion of Morel and Anderson, and $\bar{\omega}$ and ω_D are an average phonon frequency and the Debye frequency, respectively.

Using this equation for T_c reduces the problem to obtaining a more accurate calculation of the electron-phonon coupling constant λ.

ELECTRON-PHONON COUPLING CONSTANT

From Morel and Anderson[3] the electron-phonon coupling parameter is

$$\lambda = \int_{\theta_m}^{\theta_M} \frac{Z_{at}^2 N}{4M} N(0) \frac{Q^2}{\omega_Q^2} V^2(Q) \sin\theta \, d\theta, \quad (2)$$

where $N(0)$ is the density of states at the Fermi surface, N is the number of ions/cc, M is the ionic mass, Z_{at} is the ionic charge, Q is the momentum transfer $\mathbf{k}-\mathbf{k}'$, ω_Q is the corresponding phonon frequency, $V(Q)$ the Fourier transform of the electron-electron potential, and θ is the angle between $\mathbf{k}$ and $\mathbf{k}'$. This equation gives the contribution of both normal and umklapp processes. The integral is to be evaluated under the restriction that the momentum change in the scattering of electron of wave number $\mathbf{k}$ to $\mathbf{k}'$ satisfies the equation

$$\mathbf{k}-\mathbf{k}' \equiv \mathbf{Q} = \mathbf{q} \pm \mathbf{K},$$

where $\mathbf{q}$ is the phonon wave number and $\mathbf{K}$ is a reciprocal lattice vector. This equation determines the limits of integration θ_M and θ_m. A finite reciprocal lattice vector $\mathbf{K}$ denotes an umklapp process, whereas $\mathbf{K}=0$ gives the normal contribution. The total coupling constant is given by

$$\lambda = \sum_{\mathbf{K}} \lambda_{\mathbf{K}}, \quad (3)$$

where each $\lambda_{\mathbf{K}}$ is a term of the form of Eq. (2).

Taking $V(Q)$ as the Fourier transform of the screened Coulomb potential, we have

$$V(Q) = -4\pi e^2/Q^2\epsilon(Q) = -4\pi e^2/(Q^2+k_s^2), \quad (4)$$

where $\epsilon(Q) = 1+k_s^2/Q^2$ is the dielectric constant and $k_s^2 = 4\pi e^2 N(0)$ is the Fermi-Thomas screening constant. The jellium ionic plasma frequency ω_Q is equal to ω_q by the periodicity of the lattice and is given by

$$\omega_q^2 = (4\pi Z^2 e^2 N/M)[q^2/(q^2+k_s^2)]. \quad (5)$$

Noting that the scattered electrons are at the Fermi

surface, and therefore $|\mathbf{k}| = |\mathbf{k}'| = k_F$, we can write $\chi = \sin\frac{1}{2}\theta$, and find $Q^2 = 4k_F^2\chi^2$. Then using Eqs. (3)-(5), Eq. (2) becomes

$$\lambda_K = \int_{\chi_{KM}}^{\chi_{KM}} \frac{a^2}{(\chi^2+a^2)^2}\left(1+\frac{k_s^2}{q^2}\right)\chi^3 d\chi, \quad (6)$$

where $a^2 = k_s^2/4k_F^2$. For normal processes $q^2 = 4k_F^2\chi^2$, and[10]

$$\lambda_0 = \int_0^{\chi_{0M}} \frac{a^2}{\chi^2+a^2} \chi \, d\chi. \quad (7)$$

The integrals of Eqs. (6) and (7) are easily evaluated for a spherically symmetric zone structure. Since all anisotropy has been neglected in obtaining the solution to the gap equation, as well as in deriving Eq. (6), it is consistent to also neglect it here. The first step, then, is to use the spherical zone approximation[11] and replace the actual Brillouin zone by a sphere containing the same volume as the actual zone. The radius of the sphere is the Debye wave vector q_D. The reciprocal lattice[12] then appears as Fig. 1(a). We can now eliminate the remaining anisotropy of the reciprocal lattice by replacing the distribution of Brillouin zones in Fig. 1(a) by a spherically symmetric distribution as shown in Fig. 1(b). The spherical shells have midpoints at a distance K from the center and are of thickness $2q_D$. The proper phonon density of states at any momentum transfer Q is assured by a weighting function (the fractional solid angle calculated below) to be inserted in the integrand of Eq. (6).

We can calculate this weighting function in the following manner. The solid angle subtended by a given Brillouin zone (Fig. 2) at a momentum transfer Q is

$$\int_0^{2\pi}\int_{\theta_m}^{\pi} \sin\theta \, d\theta \, d\psi = 2\pi(1+\cos\theta_m),$$

where θ and ψ are the usual spherical coordinates. Now the total solid angle is 4π, and if we denote the number of zones at distance K by p_K we find that the fractional solid angle w of k space in which a momentum transfer Q with a reciprocal lattice vector K can occur is

$$w = \frac{1}{2}p_K(1+\cos\theta_m).$$

Eliminating $\cos\theta_m$ by the cosine law for triangles, w becomes

$$w = \frac{1}{2}p_K[1+(q_D^2-K^2-Q^2)/2KQ]. \quad (8)$$

The limits χ_{KM} and χ_{Km} are, in the spherical zone

[9] W. L. McMillan, Phys. Rev. 167, 331 (1968).

[10] Morel and Anderson used an inconsistent expression for ω_q^2 [see P. G. deGennes, *Superconductivity of Metals and Alloys* (W. A. Benjamin, Inc., New York, 1966), p. 104] and therefore Eq. (7) differs from their result.

[11] H. Jones, in *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 19.

[12] The figure shown is for a {100} plane in a simple cubic lattice with k in a ⟨100⟩ direction.

model of Fig. 1(b), replaced by χ_{K+} and χ_{K-}, where

$$\chi_{K\pm} = (K \pm q_D)/2k_F.$$

The remaining step requires the replacement of q^2 in Eq. (6) by its *two-dimensional average* over the actual range of q's encountered since now K and q are colinear in the new spherical zones, i.e., the absolute value of Q is $|\mathbf{q}| \pm |\mathbf{K}|$. Therefore, we must average q^2 over the spherical shell of radius Q in zone K.

$$\langle q^2 \rangle = \int_{K-Q}^{q_D} q^3 \, dq \bigg/ \int_{K-Q}^{q_D} q \, dq$$

$$= \tfrac{1}{2}[q_D^2 + (K-Q)^2].   \quad (9)$$

Finally, defining $K \equiv \kappa q_D$, $b \equiv (4Z)^{-1/3} = q_D/2k_F$, where
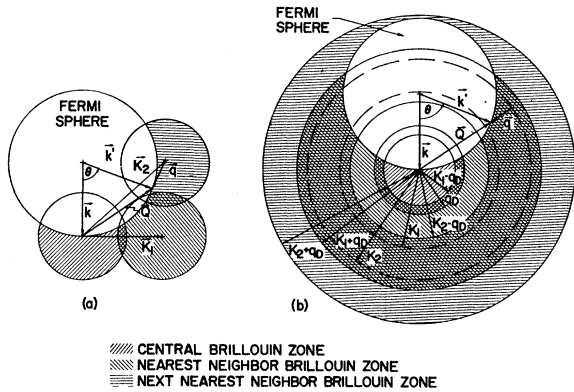

FIG. 1. Reciprocal lattice. (a) shows a section of the reciprocal lattice including the central Brillouin zone, one of the p_1 nearest zones at distance K_1, one of the p_2 next-nearest zones at K_2, and the Fermi sphere (unshaded region). (b) is the equivalent isotropic zone scheme used with the weighting function w.

Z is the valence,[13] and substituting Eqs. (8) and (9) into Eq. (6), we find

$$\lambda_K = \frac{p_K a^2}{4\kappa b} \int_{\chi_{K-}}^{\chi_{K+}} \frac{\chi^2}{(\chi^2+a^2)^2}$$

$$\times \left(1 + \frac{2a^2}{b^2+(\kappa b - \chi)^2}\right)[b^2 - (\kappa b - \chi)^2] \, d\chi. \quad (10)$$

NON-JELLIUM APPROXIMATIONS

There are two further improvements we can make to obtain a more realistic approximation to the lattice. The first is to take a pseudopotential for $V(Q)$ in Eq. (2) which includes a core-repulsion term. This replaces Eq. (4) by[14]

$$V(Q) = -[4\pi e^2/Q^2\epsilon(Q)][1 - \alpha(Q^2/q_D^2)], \quad (11)$$

[13] This defines the valence generally as the number of conduction electrons per Brillioun zone and is consistent with the usual definition for elemental metals (see Ref. 11).

[14] $\alpha = \beta q_D^2/4\pi e^2 Z_{at}$, where β is the usual pseudopotential constant. See W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).
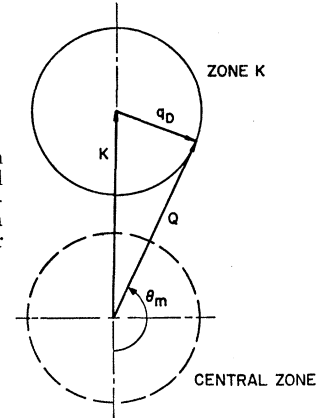

FIG. 2. Coordinate system for calculation of the fractional solid angle (weighting function) subtended by a given zone K at momentum transfer Q.

which results in an additional factor in Eq. (10) of $(1 - \alpha\chi^2/b^2)^2$. The second modification involves the use of the actual phonon velocity of sound rather than the plasma velocity of sound. The plasma velocity of sound entered through Eq. (5). In the low-frequency limit $(q\to 0)$,

$$S_p^2 = 4\pi Z^2 e^2 N/k_s^2 M.   \quad (12)$$

One then corrects for the actual sound velocity by multiplying Eq. (10) by a factor $\sigma^2 = S_p^2/S^2$, where S is the measured velocity of sound. This correction gives us the correct magnitude of the phonon frequencies involved, but keeps the simple jellium form for the dispersion relation, determined by the factor $(q^2+k_s^2)^{-1}$. In reality, of course, one must use $\sigma_L^2 =$
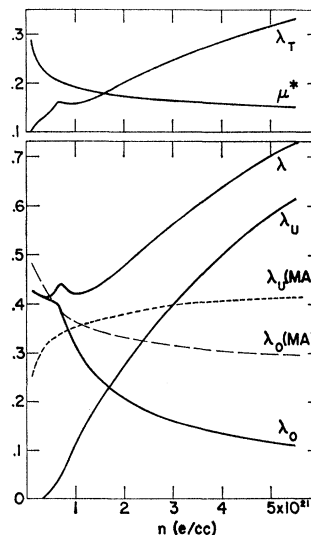

FIG. 3. Electron concentration dependence of the superconducting coupling parameters for the case of lanthanum selenide. Results are shown for both the normal (λ_0) and umklapp (λ_U) contributions to the electron-phonon interaction. The dashed curves show the Morel–Anderson results (Ref. 3) for these parameters. The curve labelled λ gives the total electron-phonon interaction. The upper two curves show the screened Coulomb repulsion (μ^*) and the net-interaction parameter (λ_T).
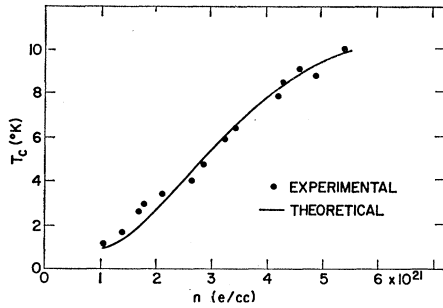
FIG. 4. Superconducting transition temperature of lanthanum selenide as a function of conduction-electron concentration.

$S_p{}^2/S_L{}^2$, where S_L is the longitudinal sound velocity, for the normal processes λ_0 and $\sigma_{\mathrm{av}}{}^2 = S_p{}^2/S_{\mathrm{av}}{}^2$, where S_{av} is the average sound velocity over the longitudinal and two transverse modes for the umklapp processes. With these additions the final expression for the umklapp terms $(K \neq 0)$ becomes

$$\lambda_K = \frac{p_K a^2 \sigma_{\mathrm{av}}{}^2}{4\kappa b} \int_{\chi_{K-}}^{\chi_{K+}} \frac{\chi^2}{(\chi^2+a^2)^2} \left(1+\frac{2a^2}{b^2+(\kappa b-\chi)^2}\right)$$

$$\times [b^2-(\kappa b-\chi)^2][1-(\alpha/b^2)\chi^2]^2 \, d\chi, \quad (13)$$

with

$$\chi_{K\pm} = b(\kappa\pm 1). \quad (14)$$

The normal contribution is

$$\lambda_0 = \sigma_L{}^2 \int_0^b \frac{a^2}{\chi^2+a^2} \left(1-\frac{\alpha}{b^2}\chi^2\right)^2 d\chi. \quad (15)$$

There is the additional condition on the upper limits that $\chi_{KM} \leq 1$. Therefore, if χ_{K+} or $b \geq 1$, it is to be replaced by 1. These integrals can be evaluated analytically, but the resulting expression is quite complicated and sheds no further light on the behavior of λ, so they will be left in this form.

The contribution of these two terms to the electron-phonon interaction is shown in Fig. 3, where the normal contribution λ_0 and the umklapp contribution λ_U [the sum of Eq. (13) over all $K \neq 0$] are plotted
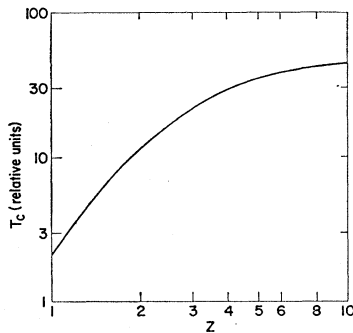

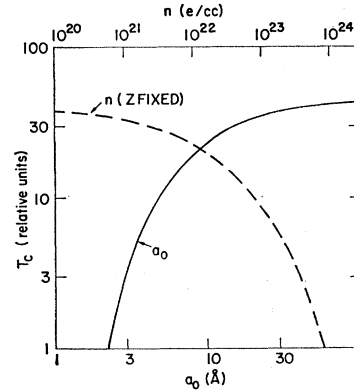FIG. 5. Dependence of transition temperature on valence.

FIG. 6. Dependence of transition temperature on lattice parameter and electron concentration at fixed valence.

as a function of electron concentration.[15] For comparison the results of using the Morel-Anderson expressions[3] are shown. The results of the present work are quite different. The reason is that the dominant effect is the change in overlap of the Fermi surface with the various Brillouin zones, which was not considered by Morel and Anderson. Since they only considered λ_0 and λ_U separately, assuming that one or the other strongly dominated, it may be more proper to compare their results to $\lambda(=\lambda_0+\lambda_U)$, which is also shown in Fig. 3. This curve still differs appreciably from Morel-Anderson.

The upper two curves in this figure show the screened Coulomb repulsion μ^* [Eq. (16)] and the total interaction parameter λ_T, which is just the inverse of the exponent in Eq. (1) and is essentially a net superconducting coupling constant. This latter curve shows some rather interesting behavior in that below 10^{21} e/cc the slope of the curve decreases, and a small bump appears before λ_T proceeds to decline again below about 5×10^{20} e/cc. This peak, which is even more
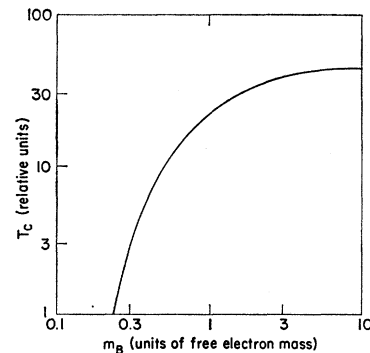

FIG. 7. Dependence of transition temperature on effective mass.

[15] The parameters used in evaluating Eqs. (13)–(15) are those suitable to lanthanum selenide (see next section and Ref. 8). As discussed in the last section of this paper, it is not possible to display a simple curve demonstrating all the implications of these equations.

striking on the curve for λ, arises from the change in slope of the λ_0 curve which occurs when, finally, the whole Fermi surface lies within the central Brillouin zone, and the disappearance of the umklapp contribution which occurs when the Fermi surface ceases to overlap any higher-order zones. The bump is attenuated somewhat on the λ_T curve since in the region of electron density where the bump occurs μ^* is also beginning to increase rapidly. This bump has not yet been observed experimentally. The measurements discussed in the next section extend down to only 1°K and therefore above the region of the bump (see Fig. 4).

LANTHANUM SELENIDE

We are now prepared to calculate T_c directly from Eq. (1). Lanthanum selenide will be used as a test case since it appears that it is a fairly simple superconducting system and allows a measurement of T_c as a function of electron concentration.[8] The study of
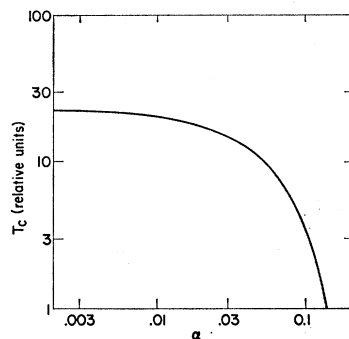
FIG. 8. Dependence of transition temperature on the pseudopotential core repulsion.

this functional dependence provides a more reliable comparison with experiment than the single point obtained in predicting T_c for an element.

In order to determine T_c we must know[16] the electron concentration n, band mass m_B, S_L, S_{av}, α, θ_D, the lattice parameter a_0, and the crystal structure. The Coulomb repulsion as well as λ can be calculated from these parameters.[17] It is given by Morel and Anderson[3] as

$$\mu^*=\mu/(1+\mu \ln E_F/k\Theta_D),   (16)$$

where E_F is the Fermi energy and

$$\mu=\tfrac{1}{2}a^2 \ln(1+a^2/a^2).   (17)$$

All the above parameters except α, S_L, and S_{av} have been experimentally determined.[8] These latter parameters are obtained by first assuming $S_L=S_{av}=S$ and

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[16] These parameters are sufficient to determine all the quantities in Eqs. (13)–(15). q_D and K are determined by a_0 and the crystal structure (see Ref. 11), b is found from q_D and $k_F=(3\pi^2n)^{1/3}$, and a^2 is obtained from k_F^2 and $ks^2=4\pi e^2N(0)=16\pi e^2 m_B k_F/h^2$.

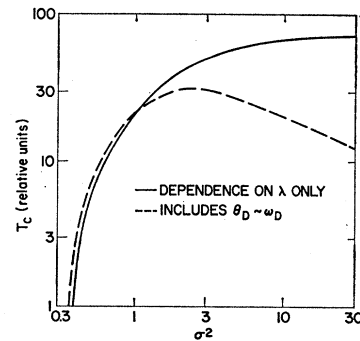[17] The behavior of λ and μ^* for these parameters was discussed in the previous section and is shown in Fig. 3.

FIG. 9. Dependence of transition temperature on velocity of sound. The solid curve takes into account the velocity of sound dependence of λ only. The dashed curve includes the dependence of Θ_D on ω_D (and thereby on the velocity of sound).

then finding S and α by fitting T_c and the slope of T_c versus n at the point $n=5\times10^{21}$ e/cc. The results are in Fig. 4, where the theory is shown as the solid line along with the experimental points. The values obtained for the parameters[18] are

$$\alpha=0.08,   S=4.3\times10^5 \text{ cm/sec}.$$

We cannot say much about the value for α since no pseudopotential calculations have been performed for a material such as lanthanum selenide. It is a reasonable value however, being within 10% of the value calculated for the simple bcc metal, sodium. The value for S is also very reasonable for the velocity of sound in a solid.

DISCUSSION

The expression for λ is too complex for one to determine easily by inspection the behavior of T_c as a function of its various parameters. To get a feel for the behavior of the theory, we can calculate T_c as a function of the various parameters and then present the curves of these results. This does not necessarily illustrate all the possible situations since the curve of T_c as a function of parameter 1 can in principle be a strong function of the constant values chosen for parameters 2, 3, etc. Nevertheless, plots of this kind will certainly give some insight into the behavior of T_c. The curves presented in Figs. 5–9 are calculated using the parameters given in Table I (exclusive of the

TABLE I. Values of the parameters used to calculate the functional dependence of T_c.

$n=10^{22}$ e/cc	$m_B=1$ electron mass
$Z=2$	$\sigma=1$
$a_0=6$ Å	$\alpha=0$

[18] The measured values (see Ref. 8) of the parameters used in the calculation are $m_B=1.3$, $a_0=9.049$ Å, and $\Theta_D=193°K$. The crystal structure is bcc.

parameter being varied). From these curves one sees that any parameter may be of great importance (i.e., there is a region of large slope in the curve for all parameters), and one cannot easily make any general statements of the importance of one parameter or the other without a careful evaluation of all parameters for the substance in question. It is clear, however, that for lanthanum selenide the parameters to which T_c is most sensitive are α and Z.[19] A change of 10% in α causes a change of about 20% in T_c. For the superconducting elements, on the other hand, it would appear that a_0, m_B, and α are of greatest importance. Regularities in the dependence of superconductivity on material parameters were pointed out by Matthias[1,20] about 10 years ago. In particular, the valence dependence he observed is in good agreement with that shown in Fig. 5 and the dependence on lattice parameter[21] is accounted for by the curve in Fig. 6.

[19] For La_3Se_4, $Z=2$, and $n=5.4\times10^{21}$ e/cc. Z varies as $2n/n(La_3Se_4)$ across the lanthanum selenide series (see Ref. 8).
[20] B. T. Matthias, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1957), Vol. 11.
[21] Matthias and Pines discuss the interelectron spacing r_s which is just $r_s=a_0/Z$.

In closing, it is interesting to observe that in spite of the simplicity of their approximations, Morel and Anderson[3] did obtain, for the most part, reasonable values for T_c. This is due to the fact that the two largest corrections to their calculation tend to cancel. They underestimated λ but used the weak coupling equation

$$T_c \simeq \Theta_D \exp[-1/(\lambda-\mu^*)],$$

which overestimates the value for T_c for a given λ.

The agreement obtained here in the lanthanum-selenide case should give us enough confidence to try to apply the theory to other systems. Also, it is clear that further improvements, such as taking into account more complicated band or phonon structures, can be made.[22]

ACKNOWLEDGMENT

I would like to thank Dr. J. F. Janak for many interesting and informative discussions.

[22] J. F. Janak is presently carrying out calculations for the elements which include a more detailed examination of the phonon structure (private communication).

Superconductivity in the Lanthanum Selenide System

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(Received 15 June 1967)

Lanthanum selenide has been found to be a very good system in which to investigate the dependence of superconductivity on various material parameters, since in this system one can vary these parameters in a relatively independent manner. This investigation reports on the behavior of the superconducting transition temperature as a function of electron concentration and on measurements of some relevant electronic and lattice properties of the system. Crystallographic, Hall-effect, Pauli-susceptibility, and specific-heat measurements have been made and were found to be in accord with a model of lanthanum selenide as a free-electron-like metal. Using this model, the electron-concentration dependence of the transition temperature was calculated and found to be in excellent agreement with experiment over the whole experimentally measured range of 1 to 10°K, corresponding to a variation of electron concentration between 0.8 and 5.4×10^{21} electrons/cc.

INTRODUCTION

LANTHANUM selenide (La_3Se_4) has been shown to be a superconductor with a transition temperature of 10°K.[1,2] This material has the thorium phosphide crystal structure and is isostructural with gadolinium selenide, which has proven to be a very fruitful system for magnetic studies.[3] Since we believed that the

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[1] R. M. Bozorth, F. Holtzberg, and S. Methfessel, Phys. Rev. Letters 14, 952 (1965).
[2] P. E. Seiden and F. Holtzberg, in *Proceedings of the Tenth International Conference on Low-Temperature Physics, Moscow, 1966*. (Proizvodstrenno-Izdatel'skii Kombinat, VINITI, Moscow, 1967).
[3] F. Holtzberg, T. R. McGuire, S. Methfessel, and J. C. Suits, J. Appl. Phys. 35, 1033 (1965).

electronic properties which made the magnetic system of interest would also be present in the superconducting one, we decided to carry out a systematic investigation of this system. We had hopes that this investigation would provide an extensive quantitative check on the theory of superconductivity. As we will show here this has indeed been the case.

The main properties that make lanthanum selenide an unusually interesting system are the following. Firstly, the two materials La_3Se_4 and La_2Se_3 have the same crystal structure and *lattice parameter*. Secondly, one can prepare a continuous series of solid solutions between these two end members without any change in crystal structure or lattice parameter. We may write the composition as $La_{3-x}[\ ]_xSe_4$, where $[\ ]$ denotes a vacancy and $0 \leq x \leq \frac{1}{3}$. La_3Se_4 is metallic while La_2Se_3