

Fourier Coefficients of Crystal Potentials*

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A method is developed for the calculation of the Fourier coefficients of the electrostatic potential of a given distribution of valence electrons in a solid. The valence electron wave functions are expressed as combinations of orthogonalized plane waves. The treatment takes full account of the nonspherical character of the atomic polyhedron. Application is made to lithium.

INTRODUCTION

AN important problem in the calculation of electronic energy bands in solids is the determination of the crystal potential. Most existing calculations assume that the potential energy is spherically symmetric inside an atomic polyhedron.¹ This approximation may be serious for the valence electron distribution in multivalent solids. A method for determining the electrostatic potential of a given charge distribution taking the correct crystal symmetry into account should be quite useful.

For example, consider the simple case of a uniform distribution of valence electrons in a cubic solid. The approximation is often made that this distribution is equivalent to that of uniformly charged spheres (whose radius is chosen so that the volume of the sphere is equal to that of the actual cell). The potential of such a charge sphere can easily be computed. But the sphere approximation is not self consistent. Such spheres, placed on atomic sites, would overlap in some regions of the atomic cell and not touch in others so that twice the charge desired is present in some places and none at all in others. Thus it is not surprising that in a Fourier analysis of this potential there are nonzero coefficients $V(\mathbf{k})$ for $\mathbf{k} \neq 0$. On the other hand, the potential of a really uniform charge distribution would have to be constant, and have no nonzero Fourier coefficients for $\mathbf{k} \neq 0$.

Heine has attempted to determine a correction potential to be added to the uniform sphere result to take account of the nonspherical nature of the actual distribution.² His method seems, however, to be unnecessarily cumbersome. Our approach is based on the fact that in the orthogonalized plane wave (OPW) method of calculating energy bands, it is principally the Fourier coefficients of the crystal potential which must be determined.^{3,4}

In this work a method is presented for calculation of

the Fourier coefficients of the crystal potential from the expansion coefficients of the wave functions when they are expressed as sums of orthogonalized plane waves. Application is made to lithium.

PROCEDURE

Let the charge distribution in the crystal, including electrons and nuclei be expressed by the function $e\rho(\mathbf{r})$. The potential energy $V(\mathbf{r})$ of an electron (charge $-e$) at $\mathbf{r}$ is determined from Poisson's equation.

$$\nabla^2 V = +8\pi\rho. \quad (1)$$

We use atomic units with energy measured in Rydbergs. The $+$ sign indicates that $V(\mathbf{r})$ will be negative for an attractive potential. The potential and charge density are expressed in terms of their Fourier components:

$$\begin{aligned} V(\mathbf{r}) &= \sum_{\mathbf{h}} V(\mathbf{h}) \exp(i\mathbf{h} \cdot \mathbf{r}), \\ \rho(\mathbf{r}) &= \sum_{\mathbf{h}} \rho(\mathbf{h}) \exp(i\mathbf{h} \cdot \mathbf{r}). \end{aligned} \quad (2)$$

In (2), the sums run over all reciprocal lattice vectors $\mathbf{h}$. The Fourier coefficients $V(\mathbf{h})$ are given by

$$V(\mathbf{h}) = \frac{1}{N\Omega_0} \int V(\mathbf{r}) \exp(-i\mathbf{h} \cdot \mathbf{r}) d^3r, \quad (3)$$

and similarly for $\rho(\mathbf{h})$. In (3), N is the number of unit cells in the crystal. Each unit cell has volume Ω_0 . The integration goes over the entire volume of the crystal. Upon substitution of (2) into (1), it is found that

$$V(\mathbf{h}) = -\frac{8\pi}{h^2} \rho(\mathbf{h}) = -\frac{8\pi}{N\Omega_0 h^2} \int \rho(\mathbf{r}) \exp(-i\mathbf{h} \cdot \mathbf{r}) d^3r. \quad (4)$$

This relation will be used to compute $V(\mathbf{h})$. It can easily be shown, by application of Green's theorem to Poisson's equation that (4) is valid provided the normal component of ∇V vanishes on the surface of an atomic polyhedron.⁵ Essentially this condition is required by symmetry for a cubic solid with inversion symmetry. It appears to have been ignored in some calculations.

The charge density must be the same in each cell. Consequently we write it as a sum of the charges in each unit cell

$$\rho(\mathbf{r}) = \sum_{\mu} \sigma(\mathbf{r} - \mathbf{r}_{\mu}), \quad (5)$$

⁵ More precisely, the integral $\oint e^{i\mathbf{k} \cdot \mathbf{r}} \nabla V \cdot d\mathbf{S}$ over the surface of the polyhedron is required to vanish.

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¹ For a review of band calculations see J. Callaway, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7.

² V. Heine, Proc. Roy. Soc. (London) A240, 363 (1957).

³ For a review of the OPW method see, T. O. Woodruff, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4, p. 367.

⁴ J. Callaway, Phys. Rev. 97, 933 (1955).

where $\sigma(\mathbf{r}-\mathbf{r}_\mu)$ differs from zero only in the cell which is located at $\mathbf{r}_\mu$.

On substitution of (5) into (4), we find

$$V(\mathbf{h}) = -\frac{8\pi}{N\Omega_0\hbar^2} \sum_{\mu} \exp(-i\mathbf{h}\cdot\mathbf{r}_\mu) \int_{\Omega_0} \sigma(\mathbf{r}) \exp(i\mathbf{h}\cdot\mathbf{r}) d^3r,$$

the integral being restricted to the central unit cell only.

The lattice sum is

$$\sum \exp(-i\mathbf{h}\cdot\mathbf{r}_\mu) = N$$

if $\mathbf{h}$ is zero or a reciprocal lattice vector and is zero otherwise. Thus

$$V(\mathbf{h}) = -\frac{8\pi}{\Omega_0\hbar^2} \int_{\Omega_0} \sigma(\mathbf{r}) \exp(-i\mathbf{h}\cdot\mathbf{r}) d^3r. \quad (6)$$

In order to simplify the discussion, we consider in the remainder of this paper only monatomic cubic solids containing one atom per unit cell. The atom consists of a point charge of charge number Z and a continuous electron distribution σ_e . The cell is electrically neutral.

$$\sigma(\mathbf{r}) = Z\delta(\mathbf{r}) - \sigma_e(\mathbf{r}), \quad (7)$$

where

$$\int \sigma_e(\mathbf{r}) d^3r = Z.$$

It is useful to separate the electron distribution into two parts: the core electrons and the valence electrons. It will be assumed that the wave functions of the core electrons go to zero before the cell boundary is reached. Consequently the Fourier coefficients of the potential of these electrons may be computed accurately from Eq. (6) in the usual approximation in which the cell is replaced by the sphere of equal volume.

The valence electron distribution requires more careful treatment. If $u_{\mathbf{k}}$ is the periodic part of a Bloch wave function

$$\psi_{\mathbf{k}} = N^{-1/2} e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}),$$

the valence charge density σ_v is

$$\sigma_v = \sum_{\mathbf{k}} |u_{\mathbf{k}}|^2 \quad (8)$$

(which we consider to be defined in one cell only). The sum runs over all occupied $\mathbf{k}$ states. In the remainder of this calculation, we shall assume that all the valence electrons have the same $u_{\mathbf{k}}$ and that there is one valence electron per atom so

$$\int_{\Omega_0} \sigma_v d^3r = \int_{\Omega_0} |u|^2 d^3r = 1. \quad (8a)$$

These restrictions can easily be removed if desired.

We consider first the Fourier coefficients for $h \neq 0$ according to Eq. (6), focussing our attention on the Fourier coefficients of the electrostatic potential of the

valence electrons: $V_v(h)$. The case $h=0$

$$V_v(\mathbf{h}) = \frac{8\pi}{\Omega_0\hbar^2} \int_{\Omega_0} |u(\mathbf{r})|^2 \exp(-i\mathbf{h}\cdot\mathbf{r}) d^3r \quad (9)$$

obviously requires special treatment. According to the assumptions above, $u(\mathbf{r})$ is the wave function for the electron state of $\mathbf{k}=0$. We expand this in orthogonalized plane waves

$$U(\mathbf{r}) = \sum_{\mathbf{g}} a(\mathbf{g}) X(\mathbf{g}), \quad (10)$$

where

$$X(\mathbf{g}) = \frac{\exp(i\mathbf{g}\cdot\mathbf{r})}{\Omega_0^{1/2}} - \sum_j \mu(\mathbf{g},j) \phi_j(\mathbf{r}), \quad (11)$$

ϕ_j is the wave function for the core state j and $\mu(\mathbf{g},j)$, the orthogonality coefficient, is

$$\mu(\mathbf{g},j) = \frac{1}{\Omega_0^{1/2}} \int \exp(i\mathbf{g}\cdot\mathbf{r}) \phi_j^*(\mathbf{r}) d^3r.$$

Note that in accord with Eq. (5), these functions are considered in one cell only. We now substitute (10) and (11) in (9) and evaluate the integral. The result is

$$\begin{aligned} V_v(\mathbf{h}) = & \frac{8\pi}{\Omega_0\hbar^2} \sum_{\mathbf{g},\mathbf{k}} a^*(\mathbf{k}) a(\mathbf{g}) \{ \delta_{\mathbf{g},\mathbf{k}+\mathbf{h}} \\ & - \sum_j [\mu^*(\mathbf{k},j) \mu(\mathbf{g}-\mathbf{h},j) + \mu(\mathbf{g},j) \mu^*(\mathbf{k}+\mathbf{h},j)] \\ & + \sum_{j,j'} \mu^*(\mathbf{k},j) \mu(\mathbf{g},j') K(\mathbf{h},jj') \}, \end{aligned} \quad (12)$$

in which

$$K(\mathbf{h},jj') = \int \phi_j^*(\mathbf{r}) \exp(-i\mathbf{h}\cdot\mathbf{r}) \phi_{j'}(\mathbf{r}) d^3r. \quad (13)$$

The integrals $K(\mathbf{h},jj')$ can be expressed in terms of the $\mu(\mathbf{k},j)$ through the properties of Fourier series, but it does not seem advisable to do this because of the relatively poor convergence of the Fourier representation of a core electron wave function. It is simpler to compute the integrals as required.

The second and third terms of Eq. (12) are easily reduced to forms involving radial integrals as is done in reference 4. We replace the core index j by the appropriate n, l , and m of the usual notation, and define

$$I(k,nl) = \int R_{nl}(r) j_l(kr) r^2 dr,$$

where R_{nl} is the radial part of the wave function for the core state j normalized so that

$$\int R_{nl}^2(r) r^2 dr = 1.$$

We obtain

$$V_v(\mathbf{h}) = \frac{8\pi}{\Omega_0 \mathbf{h}^2} \sum_{\mathbf{g}, \mathbf{k}} a^*(\mathbf{k}) a(\mathbf{g}) \left\{ \delta_{\mathbf{g}, \mathbf{k}+\mathbf{h}} - \sum_{nl} \left[\frac{4\pi}{\Omega_0} (2l+1) \right] \right. \\ \times [P_l(\cos\theta_{\mathbf{k}, \mathbf{g}-\mathbf{h}}) I(|\mathbf{k}|, nl) I(|\mathbf{g}-\mathbf{h}|, nl) \\ \left. + P_l(\cos\theta_{\mathbf{g}, \mathbf{k}+\mathbf{h}}) I(|\mathbf{g}|, nl) I(|\mathbf{k}+\mathbf{h}|, nl) \right] \\ \left. + \sum_{jj'} \mu^*(\mathbf{k}, j) \mu(\mathbf{g}, j') K(\mathbf{h}, jj') \right\} \quad (14)$$

$\theta_{\mathbf{k}, \mathbf{g}}$ is the angle between the vectors $\mathbf{k}$ and $\mathbf{g}$. The Legendre polynomial P_l is normalized so that $P_l(0)=1$. The last term of (14) involves sums of products of three spherical harmonics. It does not appear desirable to give a general reduction of this term for arbitrary l , but rather to work it out for each case desired.

In the special case where there is only one core function of s symmetry, as applies in lithium, Eq. (14) takes the simpler form:

$$V_v(\mathbf{h}) = \frac{8\pi}{\Omega_0 \mathbf{h}^2} \sum_{\mathbf{g}, \mathbf{k}} a^*(\mathbf{k}) a(\mathbf{g}) \left\{ \delta_{\mathbf{g}, \mathbf{k}+\mathbf{h}} - \frac{4\pi}{\Omega_0} [I(k) I(|\mathbf{g}-\mathbf{h}|) \right. \\ \left. + I(g) I(|\mathbf{k}+\mathbf{h}|)] + \frac{4\pi}{\Omega_0} I(k) I(g) Q(h) \right\}. \quad (15)$$

In which $I(k) = I(k10)$ and

$$Q(h) = \int R_{10^2}(r) j_{\frac{1}{2}}(hr) r^2 dr.$$

AVERAGE CRYSTAL POTENTIAL

The Fourier coefficient of potential $V(\mathbf{h})$ for $h=0$, which gives the volume average of the crystal potential, requires special treatment. The general procedure is the same as employed by Birman⁶ and many others. We define

$$V(0) = \lim_{\mathbf{h} \rightarrow 0} V(\mathbf{h}) = \lim_{\mathbf{h} \rightarrow 0} \left(-\frac{8\pi}{\Omega_0 \mathbf{h}^2} \int \sigma(\mathbf{r}) \exp(-i\mathbf{h} \cdot \mathbf{r}) d^3\mathbf{r} \right). \quad (16)$$

This limit can easily be shown to exist if the cell is electrically neutral and the charge distribution has inversion symmetry.

In evaluating (16) we will neglect the core electrons since their contribution can be determined in the spherical approximation, and consider a neutral charge distribution consisting of a point charge of $Z=1$ and one valence electron as in Eq. (8a). Our procedure is to expand $\exp(-i\mathbf{h} \cdot \mathbf{r})$ in powers of h , including terms of order h^2 .

⁶ J. L. Birman, Phys. Rev. **98**, 1863 (1955).

$$V(0) = \lim_{h \rightarrow 0} \left(-\frac{8\pi}{\Omega_0 h^2} \int_{\Omega_0} \sigma(\mathbf{r}) [1 - i\mathbf{h} \cdot \mathbf{r} \cos\theta - \frac{1}{2} h^2 r^2 \cos^2\theta + \dots] d^3\mathbf{r} \right).$$

We have

$$\int_{\Omega_0} \sigma(\mathbf{r}) d^3\mathbf{r} = 0$$

because the charge distribution is neutral, and

$$\int \sigma(\mathbf{r}) r \cos\theta d^3\mathbf{r} = 0$$

because of inversion symmetry. Thus

$$V(0) = +\frac{4\pi}{\Omega_0} \int_{\Omega_0} \sigma(\mathbf{r}) r^2 \cos^2\theta d^3\mathbf{r}. \quad (17)$$

Because of the factor r^2 in (17), the point charge at the center does not contribute, so by (7)

$$V(0) = -\frac{4\pi}{\Omega_0} \int_{\Omega_0} \sigma_v(\mathbf{r}) r^2 \cos^2\theta d^3\mathbf{r}. \quad (18)$$

We can make use of the assumed cubic symmetry of σ_v to simplify (18) further. We have

$$\cos^2\theta = \frac{1}{3} + \frac{2}{3} P_2(\cos\theta),$$

where P_2 is the second Legendre polynomial. P_2 belongs to the representation Γ_{12} of the cubic point group⁷ whereas σ_v has Γ_1 symmetry so that the integral with P_2 vanishes. Thus

$$V(0) = -\frac{4\pi}{3\Omega_0} \int_{\Omega_0} \sigma_v(\mathbf{r}) r^2 d^3\mathbf{r}. \quad (19)$$

For the special case of a uniform charge distribution, $\sigma_v = \Omega_0^{-1}$. We have

$$V(0) = -\frac{4\pi}{3\Omega_0^2} \int_{\Omega_0} r^2 d^3\mathbf{r}. \quad (20)$$

In the approximation that the cell is a sphere of radius r_s , $V(0)$ becomes

$$V(0) = -3/5r_s, \quad (21)$$

which is a well-known result. The result of (20) using the actual polyhedral cell will be larger in magnitude than the result (21).

We now expand σ_v in orthogonalized plane waves according to (8), (10), and (11), substitute into (19) and perform the integral. The result can be written in

⁷ F. C. Von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947); Bouckaert, Smoluchowski, and Wigner, Phys. Rev. **50**, 58 (1936).

TABLE I. Normalized eigenvector for lithium. The quantities $N_{\mathbf{h}}$ and $(N_{\mathbf{h}})^{1/2}a(\mathbf{h})$ are given for each plane wave type employed, where $N_{\mathbf{h}}$ is the number of waves of the particular type and $a(\mathbf{h})$ is the expansion coefficient in Eq. (10). The wave type (lmn) signifies the waves employed are of the form $\exp[2\pi i(\pm lx \pm my \pm nz)]$.

Wave type	$N_{\mathbf{h}}$	$N_{\mathbf{h}}^{1/2}a(\mathbf{h})$
000	1	1.03452
110	12	-0.03169
200	6	-0.07439
211	24	-0.04076
220	12	-0.00162
310	24	-0.00300
222	8	-0.00350
321	48	-0.00546

the following way

$$V(0) = -\frac{4\pi}{3\Omega_0} \sum_{\mathbf{k}, \mathbf{g}} a^*(\mathbf{k})a(\mathbf{g}) \left\{ H(\mathbf{g}-\mathbf{k}) - \sum_j [\mu^*(\mathbf{k}, j)\nu(\mathbf{g}, j) + \nu^*(\mathbf{k}, j)\mu(\mathbf{g}, j)] + \sum_{jj'} \mu^*(\mathbf{k}, j)\mu(\mathbf{g}, j)\lambda(jj') \right\}, \quad (22)$$

in which

$$\nu(\mathbf{g}, j) = \Omega_0^{-1/2} \int \exp(i\mathbf{g} \cdot \mathbf{r}) \phi_j^*(\mathbf{r}) r^2 d^3\mathbf{r},$$

$$\lambda(j, j') = \int \phi_j^*(\mathbf{r}) \phi_{j'}(\mathbf{r}) r^2 d^3\mathbf{r},$$

$$H(\mathbf{g}-\mathbf{k}) = \Omega_0^{-1} \int \cos[(\mathbf{g}-\mathbf{k}) \cdot \mathbf{r}] r^2 d^3\mathbf{r}.$$

This form can easily be reduced to involve only radial integrals, except for H , according to the procedures of reference 4 providing that the core functions ϕ_j are zero on the cell boundary. Define

$$J(k, nl) = \int R_{nl}(r) j_l(kr) r^4 dr,$$

and

$$S(n, n'l) = \int R_{n'l} R_n r^4 dr.$$

Then (22) becomes

$$V(0) = -\frac{4\pi}{3\Omega_0} \sum_{\mathbf{k}, \mathbf{g}} a^*(\mathbf{k})a(\mathbf{g}) \left\{ H(\mathbf{g}-\mathbf{k}) - \sum_{nl} \left[\frac{4\pi}{\Omega_0} (2l+1) P_l(\cos\theta_{\mathbf{k}\mathbf{g}}) \right] \times [I(k, nl)J(g, nl) + I(g, nl)J(k, nl) - \sum_{n'} I(k, n'l)I(g, nl)S(n, n'l)] \right\}. \quad (23)$$

Finally, in the special case where there is only one core

state of s symmetry, the result is:

$$V(0) = -\frac{4\pi}{3\Omega_0} \sum_{\mathbf{k}, \mathbf{g}} a^*(\mathbf{k})a(\mathbf{g}) \left\{ H(\mathbf{g}-\mathbf{k}) - \frac{4\pi}{\Omega_0} [I(k)J(g) + I(g)J(k) - I(k)I(g)S] \right\}, \quad (24)$$

in which $J(g) = J(g, 10)$, $S = S(11, 0)$.

APPLICATION TO LITHIUM

We have computed the Fourier coefficients of the valence electron potential $V_v(\mathbf{h})$ for lithium and also the average potential $V(0)$ of such a distribution neutralized by a unit point charge in each cell, according to Eqs. (15) and (24). The computation is based on the band structure calculation of Glasser and Callaway.⁸ The valence electron wave function was taken to be the eigenvector of the eighth-order matrix problem for the state Γ_1 . The normalized eigenvector is given in Table I. The computed Fourier coefficients are given in Table II, where they are compared with those obtained for a uniform charge distribution in the spherical approximation [set $u = \Omega_0^{-1/2}$ in (9) and replace the cell by a sphere of radius r_s].

In the computation of $V(0)$ the integral $\int_{\Omega_0} r^2 d^3\mathbf{r}$ was transformed by Gauss' theorem into a surface integral over the surface of the polyhedral cell. We obtain

$$\Omega_0^{-1} \int_{\Omega_0} r^2 d^3\mathbf{r} = \frac{\sqrt{221}}{100} a^2 = 0.1487a^2,$$

where a is the lattice constant such that the cell volume is $a^3/2$. This result is applicable to any body-centered cubic solid. A mesh integration using 505 points in one forty-eighth of the cell gave a result in excellent agreement with this. For comparison, if the cell is replaced by the sphere of the equal volume, the result is $0.1455a^2$. The difference is about 2%. The small difference indicated to us that sufficient accuracy would be obtained if the integrals $H(\mathbf{k})$ for $\mathbf{k} \neq 0$ were computed in the spherical approximation, which was done.

The small values of the $V_v(\mathbf{h})$ for $\mathbf{h} \neq 0$ as compared with the corresponding coefficients of the ionic potential

TABLE II. Fourier coefficients of valence electron potential for lithium. The first five coefficients $V(\mathbf{h})$ obtained from Eqs. (15) and (24) are given as functions of $n^2 = (a\mathbf{h}/2\pi)^2$. All computations are made for $a = 6.518$. In the third column are given the Fourier coefficients of a uniform charge distribution in the spherical approximation.

n^2	$V(\mathbf{h})$	$V(\mathbf{h})$ (uniform sphere)
0	-0.1998	-0.1869
2	-0.001987	+0.001763
4	-0.002027	-0.003864
6	+0.000404	-0.000247
8	+0.000777	-0.000815

⁸ M. L. Glasser and J. Callaway, Phys. Rev. **109**, 1541 (1958).

(see reference 8) indicate that inclusion of the $V_v(\mathbf{h})$ can have little effect on the relative positions of the energy levels calculated for lithium using the Seitz potential.⁹

⁹ The Seitz potential does not satisfy the condition $(\nabla V)_{r_s}=0$, and this may require a significant correction.

All these calculations have been performed for $r_s=3.21$, and a lattice constant $a=6.518$.

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Low-Temperature Influence on the Technetium-99m Lifetime*

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The rate of decay of a nuclear isomer has been demonstrated to be influenced by its electronic environment. This effect has been utilized to detect environmental changes of Tc^{99m} in its metallic lattice at low temperatures. The effect of low temperature on the decay constant of Tc^{99m} in technetium metal was measured. Measurements were made at 77°K and 4.2°K. Since the metal is superconducting at 4.2°K, a measurement was made at 4.2°K in a magnetic field sufficient to destroy superconductivity. Results of the experiments indicate a negligible change in the decay constant for the metal at 77°K, whereas a noticeable change in the decay constant was observed for the superconducting metal at 4.2°K:

$$\lambda(4.2^\circ\text{K superconducting}) - \lambda(293^\circ\text{K}) = (6.4 \pm 0.4) \times 10^{-4} \lambda(293^\circ\text{K}).$$

Measurements on the low-temperature normal-state metal indicate a gross removal of this influence:

$$\lambda(4.2^\circ\text{K normal}) - \lambda(293^\circ\text{K}) = (1.3 \pm 0.4) \times 10^{-4} \lambda(293^\circ\text{K}).$$

THE decay of a radioactive nucleus is generally quite unaffected by the physical surroundings of the nucleus. However, in two examples, the decay constant has been shown to be affected slightly by chemical surroundings, i.e., in the decay by K capture of Be^7 and in the internal conversion² of Tc^{99m} . This change in decay constant is attributed to a change in the electron density near the nucleus.

Tc^{99m} is ideally suited to this type of experiment because of its extremely small isomeric transition energy of 2 kev. This low transition energy insures interaction with electrons only beyond the second shell where they may be more easily affected by external means. Since technetium has been found to be a superconductor,³ it was decided that an investigation of the decay constant at low temperatures might be of interest.

I. THE EXPERIMENT

The method employed for the measurement of minute differences of decay constant was the differential method of Rutherford, which has been used extensively in in-

vestigations of this nature.^{1,2,4,5} Two sources whose decay constants are very nearly equal are compared by placing the sources in identical ionization chambers and measuring the difference in ion current as a function of time. The difference in their decay constants may then be found by plotting the difference current times the inverse decay factor, $\exp(\lambda t)$, against time. The slope of the straight line which best fits these data is equal to the difference in decay constant times the initial strength of one source. This calculation and the standard deviations have been discussed in complete detail in the literature.⁶

The ionization chambers used in the present work were constructed of brass tubing $7\frac{1}{2}$ in. in diameter and 15 in. long with $\frac{1}{2}$ -in. stainless steel tubes soldered in the ends to permit essentially 4π counting geometry. The chambers were filled to a pressure of 200 psi with pure aged argon. A vacuum tube electrometer was used to measure ion currents.

Metallic technetium sources were prepared by using the method outlined by Bainbridge *et al.*⁷ Tc^{99m} was chemically separated from its parent Mo^{99} , ground-state technetium was added, and an oxide of technetium was electrodeposited from this solution onto a copper-plated

* This work is described in greater detail in a thesis submitted by Don H. Byers in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the University of Kansas, 1958.

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¹ Kraushaar, Wilson, and Bainbridge, *Phys. Rev.* **90**, 610 (1953).

² Bainbridge, Goldhaber, and Wilson, *Phys. Rev.* **90**, 430 (1953).

³ J. G. Daunt and J. W. Cobble, *Phys. Rev.* **92**, 507 (1953).

⁴ Leininger, Segrè, and Wiegand, *Phys. Rev.* **81**, 280 (1951); **76**, 897 (1949).

⁵ Bouchez, Daudel, Daudel, Muxart, and Rogozinski, *J. phys. radium* **10**, 201 (1949).

⁶ See reference 2, Sec. II.

⁷ See reference 2, p. 434.