

It might turn out that the first excited state of Sr<sup>88</sup> has spin 2, even parity in accordance with the Goldhaber-Sunyar rule.<sup>7</sup> This would remove the last<sup>8</sup> of the four even-even nuclei with spin one in the first excited state which were quoted by Goldhaber and Sunyar<sup>7</sup> as exceptions to their rule.

\* Supported in part by the joint program of the AEC and ONR.

† Now with the Bartol Research Foundation, Swarthmore, Pennsylvania.

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<sup>2</sup> D. S. Ling and D. L. Falkoff, Phys. Rev. **76**, 1639 (1949).

<sup>3</sup> E. L. Brady and M. Deutsch, Phys. Rev. **74**, 1541 (1948).

<sup>4</sup> Bunker, Langer, and Moffat, Phys. Rev. **81**, 30 (1951).

<sup>5</sup> The authors are grateful to Professor M. Deutsch and Mr. T. R. Bulky of the MIT radioactivity group for their kind cooperation.

<sup>6</sup> Rose, Goertzel, and Perry, Oak Ridge National Laboratory Report ORNL 1023 (unpublished).

<sup>7</sup> M. Goldhaber and A. W. Sunyar, Phys. Rev. **83**, 906 (1951).

<sup>8</sup> Mo<sup>96</sup>, Te<sup>124</sup>, and Hg<sup>196</sup> all have spin 2, even and not spin 1, odd. See P. Preiswerk and P. Staehelin, Helv. Phys. Acta **24**, 300 (1951); P. Staehelin, Phys. Rev. **87**, 374 (1952); and F. R. Metzger, Phys. Rev. **83**, 842 (1951); **86**, 435 (1952).

## A Variational Method for Radiationless Transitions

B. H. BRANSDEN AND A. DALGARNO

Department of Physics and Department of Applied Mathematics,  
Queen's University of Belfast, Belfast, Northern Ireland

(Received July 11, 1952)

**R**ADIATIONLESS transitions are usually formulated by means of a time independent perturbation theory. Since the initial state is unstable, the corresponding wave function may be written as a sum of terms, several of which are not closed. The system formed is, therefore, analogous to a "collision complex" whose break-up may be described by a time independent theory.

Consider, in particular, the auto-ionization of an excited atomic system. Suppose  $\Psi_i(1 \cdots n)$  is a properly antisymmetrical closed wave function, normalized to unity, and  $\Psi_f(1 \cdots n)$  is a wave function describing the final (unbound) state for which the transition probability is required. Then, if only these two terms are included, the total wave function  $\Psi$  corresponding to an energy  $E$  may be written as the linear combination

$$\Psi = c\Psi_i + d\Psi_f,$$

where the correct  $\Psi$  satisfies the appropriate Schrödinger equation

$$(H - E)\Psi = 0;$$

$c, d$  are constants and  $\Psi_f \sim \chi(2 \cdots n)\phi(1)\sigma(1 \cdots n)$ , where  $\chi(2 \cdots n)$  is the core wave function  $\sigma(1 \cdots n)$  the spin wave function for the whole system, and  $\phi(1)$  represents an outgoing spherical wave

$$\phi(1) = r_1^{-1} \exp[i(kr_1 - \alpha \log 2kr_1)] P_l(\cos \theta).$$

$\Psi_f$  may be normalized so that

$$\int \Psi_f^*(k') \Psi_f(k) d\tau = \frac{4\pi^2}{(2l+1)} \delta(k-k'),$$

so that the constants  $c, d$  are related to  $P$ , the probability of auto-ionization per atom per unit time, by the equation

$$P = \frac{\hbar}{2m} \frac{8\pi}{(2l+1)} k \left| \frac{d}{c} \right|^2 \left( 1 + \left| \frac{d}{c} \right|^2 \right)^{-1}.$$

The variational methods developed by Hulthén<sup>1</sup> and Kohn<sup>2</sup> for collision problems may be extended for the computation of the ratio  $d/c$  and hence  $P$ . Using the notation of Kato,<sup>3</sup> we define

$$L \equiv H - E,$$

and  $\Psi_i$ , a trial wave function depending on  $p$  constants  $a_m$ , the final state wave function having the same boundary conditions as  $\Psi_f$  with the exception that  $d_i$  replaces  $d$ .

It follows that, if  $\omega \equiv \Psi_i - \Psi$ ,

$$\begin{aligned} I(a_m, d_i) &\equiv \sum_{\text{spin}} \int \Psi_i^* L[\Psi_i] d\tau \\ &= -\frac{\hbar^2}{2m} (8\pi i k) d^* (d - d_i) + \sum_{\text{spin}} \int \omega^* L[\omega] d\tau. \end{aligned}$$

This is the finite form of the usual variational equation, the integral on the right-hand side being of the order  $\omega^2$ .

Following Hulthén, we may require  $d_i - d \rightarrow 0$  and then the best function  $\Psi_i(a_m, d_i)$ , of the trial form chosen, and the best value of  $|d/c|$  may be found from the equations

$$\begin{aligned} I(a_m, d_i) &= 0, \\ & \quad m = 1, 2, \dots, p, \\ \partial I / \partial a_m &= 0, \end{aligned}$$

which (as  $d_i, a_m$  need not be real) are  $(2p+2)$  in number.

Kohn's method may also be applied, leading to the equations

$$\partial I / \partial a_m = 0, \quad m = 1, 2, \dots, p,$$

$$\partial I / \partial d_i = \frac{\hbar^2}{2m} \frac{8\pi i k}{(2l+1)} d^*,$$

$$d^* d = d_i^* d_i - \frac{2m(2l+1)}{\hbar^2} \frac{1}{8\pi i k} I.$$

A comparison of these variational methods and the usual perturbation treatment is being carried out for a number of auto-ionizations undergone by helium.

The authors wish to thank Professor D. R. Bates for his interest in the problem.

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<sup>2</sup> W. Kohn, Phys. Rev. **74**, 1763 (1948).

<sup>3</sup> T. Kato, Prog. Theoret. Phys. **6**, 394 (1951).

## The Minimum of Electrical Resistance at Low Temperatures

D. K. C. MACDONALD

Division of Physics, National Research Council, Ottawa, Canada

(Received July 10, 1952)

**T**HE initial discovery<sup>1,2</sup> of a resistance minimum at low temperatures in gold has been followed since the war by increasing interest in the analogous phenomenon in other metals.<sup>3-7</sup> An extended investigation has been in progress over the past two years on alloys of Cu, Ag, and Au, and some aspects have already been reported.<sup>6</sup> More recently particular attention has been paid to a very characteristic minimum in Cu occurring generally at about 10.5°K.

The following conclusions have now been definitely established through experiments on a rather wide range of alloys specially prepared from spectrographically pure metals. As solute, elements were chosen which tend to occur as traces in very pure samples of the parent.

(1) Pure copper and gold as parent metals do not exhibit the characteristic minimum.

(2) A variety of different solute elements when alloyed with the parent metal are capable of producing the minimum.

(3) The initial introduction of an effective "impurity" causes characteristic general scattering and a proportionately increasing resistive minimum together with a corresponding rise in the temperature of the minimum. The second effect, however, "saturates" very rapidly as the appropriate concentration (in the order of  $<10^{-2}$  atomic percent to  $10^{-1}$  percent dependent on solute and solvent) is approached. Thereafter the only further effect is to provide additional random scattering while both the magnitude and location of the minimum stay constant.

(4) In particular, it has been established in the case of copper-rich alloys that: (a) oxygen, silver, and nickel as solutes do not produce the minimum; (b) tin (which enters into homogeneous solid solution) and (c) carbon, lead, and bismuth (which at best have very small solid solubility) all produce the minimum.

(5) Also in the case of copper-rich alloys, very dilute ternary solutions of carbon and tin can almost annul the minimum over a short range of solute concentration. At the same time, anomalous behavior is observed in the over-all residual resistance.<sup>8</sup> (See following letter.)

Previous theoretical proposals<sup>9-11</sup> to account for the general minimum phenomenon appear to be inadequate when considered in the light of these results.

I am grateful to Dr. W. B. Pearson for much help in the preparation of the copper alloys.

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<sup>4</sup> A. N. Gerritsen and J. O. Linde, *Physica* **17**, 573, 584 (1951).  
<sup>5</sup> E. Mendoza and J. G. Thomas, *Phil. Mag.* **42**, 291 (1951); *Proc. Intern. Conf. on Low Temp. Phys.*, Oxford, 1951, p. 39 (unpublished).  
<sup>6</sup> I. M. Templeton and D. K. C. MacDonald, *Phil. Mag.* **42**, 432 (1951); D. K. C. MacDonald, *Proc. Intern. Conf. on Low Temp. Phys.*, Oxford, 1951, p. 58 (unpublished).  
<sup>7</sup> H. E. Rorschach and M. A. Herlin, *Phys. Rev.* **81**, 467 (1951).  
<sup>8</sup> D. K. C. MacDonald and W. Pearson, *Phys. Rev.* **88**, 149(L) (1952).  
<sup>9</sup> J. C. Slater, *Phys. Rev.* **84**, 179 (1951).  
<sup>10</sup> D. K. C. MacDonald, *Phil. Mag.* **42**, 756 (1951).  
<sup>11</sup> A. N. Gerritsen and J. Korringa, *Phys. Rev.* **84**, 604 (1951).

### Residual Resistance in Dilute Copper Alloys

D. K. C. MACDONALD AND W. B. PEARSON  
*Division of Physics, National Research Council, Ottawa, Canada*  
 (Received July 10, 1952)

EXAMINATION of the resistance minimum occurring at  $\sim 10^\circ\text{K}$  in dilute alloys of copper (reported above<sup>1</sup>) demanded as a check on alloy purity and concentration the detailed investigation of the resistance ratios  $R_{4.2^\circ\text{K}}/R_{273.2^\circ\text{K}}$ , and further of  $R_{77.7^\circ\text{K}}/R_{273.2^\circ\text{K}}$  and  $R_{90.2^\circ\text{K}}/R_{273.2^\circ\text{K}}$  for comparison with the classical results of Linde.<sup>2</sup> In general such data are of fundamental value when interpreted as cross sections,<sup>3</sup> for electron scattering and prominent deviations found from Linde's results forced us to undertake a systematic investigation. It is significant that all differences found so far are in the direction of lower cross section.

After extensive tests, alumina crucibles for high vacuum melting were chosen which caused no measurable contamination. Control spectrographic and chemical analyses were conducted during the experiments.

Linde's scattering determinations were based on measurements between liquid oxygen and room temperature, dependent on an assumed validity of Matthiessen's rule. Departures from this law, however, are now well known, particularly in the case of copper, and further confirmed by our experiments.

We find the following:

(1) In order to avoid serious errors due almost certainly to oxygen contamination, the final strain-relieving anneal after rolling or drawing must be carried out in a very high continuous vacuum, the specimen being freely suspended in a glass vessel. Following this technique in our work, pure (H.S.) Hilger copper (lab. No. 11,184) always yielded  $R_{4.2^\circ\text{K}}/R_{273.2^\circ\text{K}} = 2.9(\pm 0.3) \times 10^{-3}$  over a wide range of annealing temperatures and times. On the other hand, when a rolled strip received the final anneal in a fresh crucible sealed in an evacuated silica tube, a residual resistance some fortyfold greater was found, agreeing in magnitude with the range of specific resistance variation found by Linde using his annealing technique.

(2) Present results on dilute Cu-Sn alloys with oxygen contamination suggest that the absorbed atoms provide additional scattering centers approximately proportional to the number of already present (Sn) scattering centers. Apart from the general importance of such behavior, it follows that such experiments can yield an artificially high (but approximately constant) scattering cross section. We suggest that this explains the consistent but high cross sections which follow from Linde's work in certain cases.

(3) The figure illustrates some results obtained with dilute Cu-Ni (A), Cu-Sn (B), Cu-Ag (C), and Cu-C-Sn (D), alloys. The cross sections deduced for Ni and Ag call for little comment here; in particular, the scattering by Ni agrees very well with that of Linde. However, in the case of Sn (also Sb, not shown), which differs strongly in chemical valency from copper, the scattering as discussed above is much lower than found by Linde.

The major theoretical interest involved leads us to extend the work to the solute series: Zn→As and Cd→Sb.

(4) Investigation of carbon as an impurity led to curve D in Fig. 1 obtained for Sn alloys melted in spec-pure graphite cru-

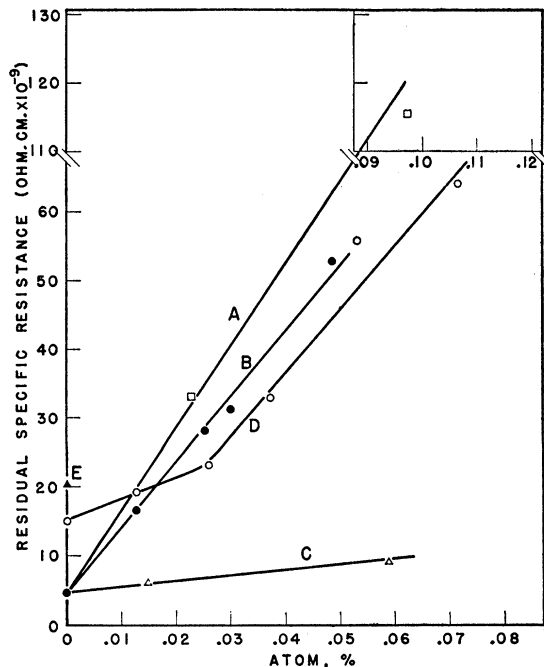


FIG. 1. Residual resistance of dilute alloys. A: Cu-Ni alloys; B: Cu-Sn alloys; C: Cu-Ag alloys; D: Cu-Sn alloys melted in spec-pure graphite crucibles; E: pure Cu melted with excess powdered graphite. (Specific resistances calculated on basis of  $1.58 \times 10^{-9}$  ohm cm for pure Cu at  $0^\circ\text{C}$ .)

cibles. That the initial additional scattering was indeed the result of carbon was confirmed by the inclusion of powdered graphite in a pure Cu melt (E). The remarkable fact emerges that, particularly for very low Sn concentrations, the scattering is far from additive. Excluding the virtually untenable hypothesis at these very low concentrations of a mutually ordered lattice structure, one is led to consider the possibility of some novel electron-ion interaction additional to the screened electrostatic potential ( $e^2e^{-ar}/r$ ) normally postulated in the theory of metallic resistance.<sup>3</sup> In view of the associated anomaly in the resistance minimum remarked above it appears possible that some type of "resonant" interaction is involved, perhaps analogous to that proposed by Gerritsen and Korringa<sup>4</sup> as a special case in Ag-Mn alloys.

We thank Mr. F. W. Richardson for able technical assistance in the above experiments.

<sup>1</sup> D. K. C. MacDonald, preceding letter, *Phys. Rev.* **88**, 148 (1952).

<sup>2</sup> J. O. Linde, *Ann. Phys.* **15**, 219 (1932).

<sup>3</sup> See, e.g., N. F. Mott, *Proc. Cambridge Phil. Soc.* **32**, 281 (1936) and N. F. Mott and H. Jones, *Properties of Metals and Alloys* (Oxford University Press, London, 1936), p. 292.

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### The Quenching-in of Lattice Vacancies in Pure Gold\*

J. W. KAUFFMAN AND J. S. KOEHLER  
*University of Illinois, Urbana, Illinois*  
 (Received August 11, 1952)

ALTHOUGH diffusion in close-packed lattices probably occurs as a result of the migration of vacancies, direct experimental evidence is meager. At present the main support for the theory stems from the Kirkendall effect<sup>1</sup> and from the agreement with