

The probabilities of the analogous transitions from 1S_0 to 3P_1 energy state in C I, N II and O III were calculated by Stevenson³ who found finite values for these probabilities. However, Stevenson does not separate the multipole radiation into the quadrupole and magnetic dipole radiation and interprets accordingly the radiation corresponding to the transitions between the energy states 1S_0 and 3P_1 as quadrupole radiation in contradiction to the $J_1 + J_2 \geq 2$ selection rule for this radiation.

Assuming the line $\lambda 4618.0$ to be due to the pure magnetic dipole radiation, the lines $\lambda 4659.4$ ($^3P_0 - ^1D_2$) and $\lambda 5312.7$ ($^3P_2 - ^1S_0$) can be explained as pure quadrupole lines and

the line $\lambda 7330$ ($^3P_1 - ^1D_2$) as due to the mixed magnetic dipole and quadrupole radiation.

We hope to confirm the above explanation of the forbidden Pb I lines by the Zeeman effect.

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³ A. F. Stevenson, Proc. Roy. Soc. A137, 298 (1932).

Concerning the Thermoelectric Effects of the Alkalis

In an extensive article,¹ I have presented an elementary treatment of the electron theory of metals in a simpler and more complete manner than I had given in my paper of 1928² and H. Bethe has followed this with a basic wave-mechanical formulation of the theory. In this note I should like to extend one phase of this treatment.

From my elementary theory the Thomson coefficient μ defined by $U = -\mu J (dT/dx)$ (U =rate of heating, J =current density), is given by

$$\mu = -\frac{\pi^2}{3} \frac{k^2}{|e|} \frac{\Lambda T}{\zeta}; \quad \Lambda = 1 + \frac{1}{2} \frac{d \log l}{d \log v} \quad (1)$$

with the simplifying assumptions that Λ and ζ are independent of T . $|e|$ is the absolute value of the charge on an electron, ζ the internal potential per electron in the Gibbs sense which I formerly denoted by W_i , l the free path, and in the expression for Λ the derivative is to be taken for the limiting velocity ($v=\bar{v}$) of the Fermi distribution. Originally I had chosen silver as an example and placed $\Lambda=1$ as a reasonable approximation. Now μ is *positive* for Cu, Ag and Au (also for Hg) and hence Eq. (1) seemed to predict the *wrong sign*. However, the alkalis rather than the noble metals are the true representatives of metals with "free" electrons. Their ionization potentials (with the exception of Li) are particularly small, their mono-valence most pronounced and the closed shell of eight electrons inside the valence electron (again excepting Li) is most clearly defined (better than the shell of eighteen electrons inside the valence electron of the noble metals).

At the time of the preparation of my *Handbuch* article measurements of the Thomson coefficients of the alkalis were not known to me. However, even at that time I could conclude from older measurements of the thermoelectric force by Bernini, et al., that, because of thermodynamic relations, the Thomson coefficient of Na and K must be negative and hence the sign required by Eq. (1) actually occurred for Na and K. In a note I postulated that reliable measurements on Rb and Cs would agree with formula (1) and expected that the comparison for Li would be less satisfactory than for the remaining alkalis.

Meanwhile my attention has been called to an article by C. C. Bidwell.³ Here measurements of the thermoelectric force are given ($\Theta_1 = d\Theta/dT$ if Θ denotes the thermoelectric

difference of potential) for the complete series of the alkalis. They show a good *linear falling off* of Θ_1 , above the melting point, if all the measurements are referred to lead as the second metal. Li is an exception and shows a *linear rise* above the melting point. Since the thermodynamic relation

$$\mu = T d\Theta_1/dT \quad (2)$$

must hold if μ is taken zero for lead, the linear decrease of Θ_1 denotes *proportionality of μ with T* and a *negative sign* as is required by Eq. (1). It is also understandable that these relations are best satisfied in the *molten state*. For the elementary theory does not take the crystal lattice into account but replaces its action schematically by a free path l , which is independent of all regularity in space. In the *solid state* Bidwell finds an α - and a β -modification. The β -modification joins at the melting point and also shows a passable linear decline of Θ_1 with T , while in the neighborhood of the melting point μ rises rather suddenly. The transition point between α and β lies at lower temperatures (-100°C for K, etc.). In the α -phase Θ_1 rises with T ; for such low temperatures, however, our elementary theory is certainly not valid.

For the molten state our formula (1) yields the *correct order and order of magnitude* of the Thomson coefficients. Table I shows this, the numbers denoting microvolts per degree. The experimental data are the values given by Bidwell in his Table III under "liquid" (denoted there by $d^2E/d\bar{v}^2$); the theoretical values are calculated from Eq. (1):

TABLE I.

	Li	Na	K	Rb	Cs
μ/T { Exp.	+0.40	-0.0282	-0.0275	-0.069	-0.062
Theor.	-0.016	-0.023	-0.036	-0.041	-0.048

Li is an exception; the remaining alkalis check surprisingly well. With respect to the order we prefer to give more credence to the theoretical numbers than to the experi-

¹ A. Sommerfeld, Handb. d. Physik 24, 2 (in press), Springer.

² A. Sommerfeld, Zeits. f. Physik 47, 1-32, 43-60 (1928).

³ C. C. Bidwell, Phys. Rev. 23, 357 (1924).

mental ones and would be inclined to look upon the departure from the natural order Na, K, . . . as unreal.

In this connection another point must be discussed, *viz.*, the magnitude of Λ . The elementary theory can make no predictions about the free path and must turn to wave mechanics for information about this point. The latter leads us to expect as the simplest possible law: l proportional to the square of the kinetic energy of the electron. From this it follows from Eq. (1) that $\Lambda=3$. This value has been used in constructing Table I. One can also readily see (compare Bethe, loc. No. 50a) that the above law relating l and Λ must hold for and only for the alkalis.

In the same manner as for the Thomson effect, the thermoelectric power of the alkalis may be calculated from the elementary theory, especially for the liquid state (Li excepted). It seems very noteworthy to me that such simple formulas as Eq. (1) (the formula for the thermoelectric effect is quite similar), at least for the simplest metals, can

predict the sign, order and magnitude approximately correctly for these complicated effects. To indicate the method of the calculations which lead to the values in Table I, I give the values of n (number of free electrons = number of metal ions per cc) and for ζ (the internal potential) in Table II. n is calculated in the usual manner from the atomic weight and density, ζ from the formula

$$\zeta = (h^2/2m)(3n/8\pi)^{2/3}. \quad (3)$$

TABLE II.

	Li	Na	K	Rb	Cs
$n \times 10^{-22}$	4.66	2.67	1.30	1.08	0.86
$\zeta \times 10^{12}$	7.4	5.1	3.2	2.8	2.4

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Magnetic Properties of Rochelle Salt

In conjunction with Müller's¹ recent note in *Physical Review* on the electric properties of Rochelle salt, it may be of interest to communicate a few tests of the magnetic properties of this substance which we have recently made. Through the courtesy of Dr. R. M. Bozorth of Bell Telephone Laboratories, a single crystal of the salt was supplied to us which in turn was cut into two smaller rectangular crystals approximately $1.2 \times 0.3 \times 0.3$ cm, the b and c axes being parallel to the long side of the rectangles respectively in the two prisms. The susceptibility along the a , b and c axes was then measured by using a Weiss magnetic balance and a field strength of about 8000 gauss. No variation in the susceptibility in these three principal directions could be found within the experimental error (half percent). The value of the mass-susceptibility was $\chi = -0.54 \times 10^{-6}$ if

$\chi_{\text{Au}} = 0.145 \times 10^{-6}$. In addition, the susceptibility at various temperatures, in the range 10°C to 30°C , for the three principal crystallographic directions was determined. No variation in the mass-susceptibility could be detected for any of the three directions to within an accuracy of about one-quarter of one percent. Apparently, therefore, the Weiss electrical field postulated by Müller to account for the anomalous behavior of the electric properties of Rochelle salt is without influence on its magnetic properties.

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¹ H. Müller, *Phys. Rev.* **44**, 854 (1933).

Periodic Unequal Potential Minima and Torsion Oscillation of Molecules

The problem of the torsion oscillation of molecules of the ethane type has been treated by Nielsen,¹ Teller and Weigert² and Koenig.³ Molecules, however, in which each of the two identical groups is composed of different atoms, as for example in the symmetric dichloroethylenes, have to be treated differently since the potential fields corresponding to the cis and the trans positions are different. The problem of the quantization of the oscillations of the two groups is reduced to solving the Hill equation $d^2\psi/d\theta^2 + (8\pi^2 I/h^2)[E - V(\theta)]\psi = 0$ in which the potential $V(\theta)$ has two unequal minima in 2π , is symmetrical about each minimum, and $V(\theta) = V(\theta + 2\pi)$ subject to the periodicity condition that $\psi(\theta) = \psi(\theta + 4\pi)$.

The fact that both the cis and the trans forms of the molecules of the type ClHC : CHCl are stable and do not transform from one to the other appreciably at low temperature justifies the assumption that the two minima are separated by a relatively large potential barrier and that

their lower energy levels lie much below the maximum value of the barrier. On this assumption the solution of the wave equation by the W-K-B method can be carried out by generalizing the cases treated by Koenig³ and the writer.⁴ For levels below the top of the potential maximum, corre-

¹ H. H. Nielsen, *Phys. Rev.* **40**, 445 (1932).

² Teller and Weigert, *Gött. Nachr.* **2**, 218 (1933).

³ H. D. Koenig, *Phys. Rev.* **44**, 675 (1933).

⁴ T. Y. Wu, *Phys. Rev.* **44**, 727 (1933). It should be made more explicit here that in the above article, there are two levels for each quantum number n , given by expressions (3), (6) and (7) corresponding to the two possible signs of δ and ϵ in Eqs. (2) and (5), namely, $\tan \delta = \pm |D/2E|$ and $\tan \epsilon = \pm |E/2D\alpha^4|$. When applied to the calculation of the F levels of heavy atoms, the atomic field is such that only the lower level in each pair, corresponding to the negative sign for δ and ϵ , is stable.