

tion that can be made from two sublattice model. (See reference above.)

(3) Owen *et al.* observed that essentially no Knight shift appears in the resonance of Mn in dilute solution in copper and silver. We have found that the gadolinium resonance shift disappears as we extend the measurement to the silver-rich alloys of palladium. The absence of these shifts cannot be explained by excessively long conduction-electron relaxation times, since we have observed no shifts even after these times were shortened by addition of paramagnetic impurities of different species into the Cu and Ag alloys. The conduction-electron interaction must still be considerable in these alloys, since the foreign atoms produced large broadenings.

(4) The  $g$  shifts observed in the Gd resonances are of negative sign. Their origin is, therefore, not the simple exchange interaction which is always positive.

Instead, we must have a polarization of mostly negative sign, in agreement with previous NMR observations. A possible mechanism for this negative polarization is the Anderson-Clogston mechanism.

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### Size Effect in Electrical Resistivity of Alloys\*

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Harrison's hypothesis on the effect of atomic size of impurities on the electrical resistance is shown to predict the resistance of alkali solutes in liquid sodium to an accuracy as high as the data warrant. The impurity resistance was calculated numerically over a range of assumed dilutions. The predicted resistance is not proportional to  $(\Delta V/V)^2$  but is approximately fitted by the empirical equation,  $\Delta\rho = \text{const}[bx - 1 + \exp(-bx)]$ , where  $x = \Delta V/V$ . New measurements on Na-K alloys are also reported.

#### INTRODUCTION

A WAY to treat the effect of atomic size of impurities on the resistivity of metals has been suggested by Harrison.<sup>1</sup> In the case of an impurity larger than the host, the dilation is regarded as lowering the positive charge density of the lattice at the scattering center. This drop in charge density creates a repulsive scattering potential for electrons.

In this paper we examine the predictions of a square potential model based on this idea. The excess resistivity  $\Delta\rho$  due to 1 at.% of solute is calculated as a function of the dilation  $\Delta V/V$ . The results, to a good approximation, obey the empirical relation,

$$\Delta\rho = \text{const}[bx - 1 + \exp(-bx)], \quad (1)$$

where  $x = \Delta V/V$ . The predictions are compared with recent measurements of the excess resistivity due to alkali solutes in liquid sodium.

Calculations of this kind have been made by Blatt,<sup>2</sup> who has tabulated the predicted excess resistivity for many solid alloys, and by Daniel,<sup>3</sup> who calculated the excess resistivity for the liquid alkali solutions just as we do here. What is new in the present work is the consideration of the form of the relation over a range of dilation, a new comparison with experiment, and the presentation of some new measurements on Na-K alloys.

#### THE MODEL

The conduction electrons are considered free except for their interaction with spherical scatterers. The potential is assumed to be square, a "well" in the case of small solutes (Li), a "barrier" for large solutes (K, Rb, and Cs). The radius of the potential is taken as the "radius" of the solute atom, as estimated from its partial molar volume in the solution.

The depth of the potential is chosen to satisfy Friedel's sum rule.<sup>4</sup> This rule is a condition on the

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<sup>1</sup> W. A. Harrison, reported in F. J. Blatt, *Phys. Rev.* **108**, 285 (1957).

<sup>2</sup> See reference 1.

<sup>3</sup> E. Daniel, *J. Phys. Chem. Solids* **13**, 353 (1960). Also see the Erratum, to be published in the same journal.

<sup>4</sup> J. Friedel, *Phil. Mag.* **43**, 155 (1952).

TABLE I. Calculated resistivity of solutes due to dilation.

Dilation $\Delta V/V$	Exact calculation $k\Delta\rho$ (at. units)	Fitted function Eq. (5) (at. units)	Difference $k\Delta\rho$ -Eq. (5) (at. units)
-0.9	10.90	11.06	-0.16
-0.8	7.80	7.66	+0.14
-0.7	5.15	5.17	-0.02
-0.6	3.24	3.36	-0.12
-0.5	1.95	2.08	-0.13
-0.4	1.09	1.19	-0.10
-0.3	0.523	0.601	-0.078
-0.2	0.216	0.241	-0.025
-0.1	0.049	0.055	-0.006
0	0	0	0
0.1	0.041	0.046	-0.005
0.2	0.150	0.167	-0.017
0.3	0.312	0.346	-0.034
0.4	0.517	0.570	-0.053
0.6	1.02	1.11	-0.09
0.8	1.61	1.72	-0.11
1.0	2.26	2.39	-0.13
1.5	4.02	4.13	-0.11
2.0	5.87	5.92	-0.05
3.0	9.61	9.54	+0.07
4.0	13.25	13.15	+0.10
5.0	16.76	16.77	-0.01

scattering phase shifts which insures that the charge on the scattering center is completely screened at large distances. The wave function for an electron at the Fermi level is analyzed into partial waves corresponding to the angular-momentum quantum number  $l=1, 2, 3, \dots$ . The phase shifts  $\delta_l$  must then obey

$$N = (2/\pi) \sum_l (2l+1) \delta_l, \quad (2)$$

where  $N$  is the scattering charge in units of the electronic charge. Friedel assumed that  $N$  was the valence difference  $Z'$  between solute and solvent. In our case, alkali solutes in sodium, this is zero.

Harrison's suggestion is to put  $N = Z' - \Delta V/V$ , to allow for the effect of the dilation  $\Delta V/V$ . Thus, we require

$$-\Delta V/V = (2/\pi) \sum_l (2l+1) \delta_l. \quad (3)$$

The calculation proceeds as follows: we choose the radius of the solute, calculate  $\Delta V/V$ , assume a trial potential depth, calculate the phase shifts, and form the Friedel sum (2). This process is iterated until (3) is satisfied sufficiently closely. In our calculations, we evaluated phase shifts up to the seventh partial wave and required that (3) hold to within  $\pm 10^{-4}$ .

The resistivity is easily found from the phase shifts. The relation is<sup>5</sup>

$$\Delta\rho = (4\pi/k) \sum_l l \sin^2(\delta_{l-1} - \delta_l), \quad (4)$$

where  $k$  is the wave number in atomic units of the Fermi electrons. For sodium,  $k=0.4740$  atomic units. The resistivity may be converted to  $\mu\text{ohm-cm/at.}\%$  by multiplying (4) by 0.217.

<sup>5</sup> P. de Faget de Casteljau and J. Friedel, J. phys. radium 17, 27 (1956).

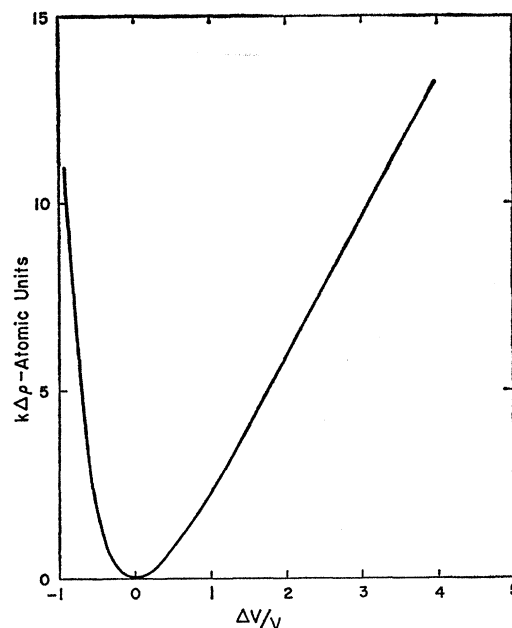


FIG. 1. Solute resistivity at 1 at.% vs dilation, 100°C.

## THE RESULTS

Table I and Fig. 1 show the results. First, note that for neither positive nor negative dilation can we support the hypothesis that  $\Delta\rho$  be proportional to  $(\Delta V/V)^2$ , as would be suggested by Linde's rule if the effect were equivalent to just an "effective valence." The relation is approximately linear for positive dilation and exponential for negative dilation. The slope is zero at the origin.

For convenience, we have fitted a two-parameter equation to the exact results as follows:

$$(k\Delta\rho)_c = a[bx - 1 + \exp(-bx)], \quad (5)$$

where  $a=1.315$  atomic units,  $b=2.75$ , and  $x=\Delta V/V$ . This equation is tabulated in Table I, together with the deviations between it and the exact results.

## COMPARISON WITH EXPERIMENT

Freedman and Robertson<sup>6</sup> have recently measured the resistivity of liquid sodium containing alkali solutes. Their results have been compared with the present theory by Daniel, with a somewhat inconclusive result.<sup>7</sup> Here we hope to give a more detailed comparison as well as to present new data on Na-K alloys.

The theory requires only one parameter for each solute, namely, its atomic volume relative to sodium. For the alkali solutes larger than sodium (K, Rb, and Cs), we have simply used the bulk densities of the pure liquids to estimate the atomic volumes. For lithium,

<sup>6</sup> J. F. Freedman and W. D. Robertson, J. Chem. Phys. 34, 769 (1961).

<sup>7</sup> See reference 3. In Daniel's original Letter, agreement was apparently good, but the erratum differs considerably.

TABLE II. Assumed densities of liquid alkali metals at 100°C and the resulting resistivity per at. % of solute in liquid sodium.

	Density (g/cm <sup>3</sup> )	$\Delta V/V$ (Na)	$\Delta\rho$ ( $\mu\text{ohm-cm/at.}\%$ )
Li	...	-0.3000 <sup>a</sup>	0.239
Na	0.9267	...	...
K	0.819	+0.92358	0.918
Rb	1.452	+1.37203	1.650
Cs	1.81	+1.95868	2.619

<sup>a</sup> Estimated by indirect means.

which is much smaller than sodium, this procedure fails badly, and the partial molar volume must be estimated by other means. The input data and resulting resistivities are tabulated in Table II. The various solutes will now be discussed in turn. The temperature in each case is 100°C.

**Lithium.** If we simply compute an atomic volume for lithium from its density, the result is about one-half the volume of a sodium atom. But the volume occupied by a lithium atom in liquid sodium must be at least as large as that of a vacancy in the liquid (assuming that the lithium goes in substitutionally).

Theoretically, we have an estimate of the size of a vacancy in solid sodium by Girifalco,<sup>8</sup> who gets a radial collapse about the vacancy of 10.8% of the normal atomic spacing. This implies a dilation of -0.29.

Experimentally, we have an estimate of the partial molar volume of lithium in liquid sodium by Salmon and Ahmann,<sup>9</sup> who measured the critical temperature of the liquid alloy with regard to miscibility. Their result is equivalent to a dilation of -0.33. Unfortunately, the result applies to solutions of 65% Li, which is the critical concentration. A measurement of the partial molar volume at low Li concentration would be very helpful.

We shall use the value -0.30 for the dilation. In Fig. 2, we show the predicted line and the data of Freedman and Robertson. The slope of the line is

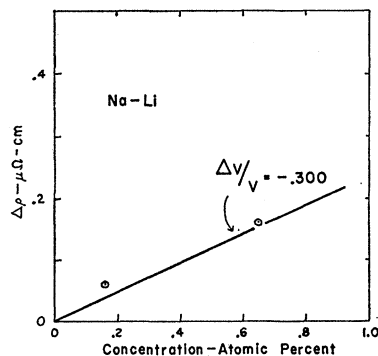


FIG. 2. Solute resistivity vs concentration for Na-Li, 100°C. In this and the succeeding graphs, the solid line is predicted by the theory. All data points (circles) are taken from reference 6.

<sup>8</sup> L. A. Girifalco and V. G. Weizer, J. Phys. Chem. Solids **12**, 260 (1960).

<sup>9</sup> O. N. Salmon and D. H. Ahmann, J. Phys. Chem. **60**, 13 (1956).

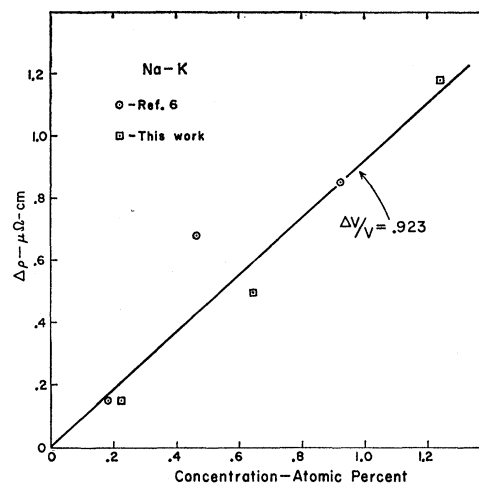


FIG. 3. Solute resistivity vs concentration for Na-K, 100°C.

calculated as follows:  $k\Delta\rho=0.523$  from Table I.  $k=0.474$  at. units at the Fermi level of Na, therefore  $\Delta\rho=1.103$  at. units  $=0.239 \mu\text{ohm-cm/at.}\%$ . The agreement is much closer than can be justified from the crude estimate of the dilation.

**Potassium.** The three points of Freedman and Robertson are shown in Fig. 3 together with our own data, whose collection is described in the Appendix. The agreement is considered good.

**Rubidium.** In rubidium, Fig. 4, we have a slightly strange result. The slope agrees well, but there appears to be a constant offset. On examining the data at higher temperatures, one sees about the same slope but with a larger offset. We regard the good agreement in the slopes as significant.

**Cesium.** Figure 5. There is a suggestion of the offset here just as in rubidium. The two rightmost points give about the same slope as predicted, but we cannot claim that this is significant. Agreement is therefore regarded as fair.

## DISCUSSION

We have shown that the quadratic relationship between the excess resistivity and the dilation, which Freedman and Robertson used to fit this data, is not to be expected from the Harrison model nor is it required by the experimental results. This brings into question the significance of their analysis in which they split the excess resistivity into dilational and core potential contributions. Although their data are quite good with regard to temperature dependence, they are still quite scattered with regard to concentration dependence, as the authors freely acknowledge in their paper. Thus, one should regard any detailed analysis of the results with some reservations.

The present calculation differs somewhat from that of Daniel<sup>3</sup> in that a numerical error is corrected and, more significantly, in that different input data are used.

Daniel calculates the atomic volume of the various solutes from the densities of the solids at 0°C; whereas we have used densities of the liquids at 100°C, except for lithium, where we estimate the partial molar volume itself. If we had used just the atomic volume of lithium, our result would be larger by a factor of three or so.

With regard to the uniform offset between the observed and predicted resistivity due to rubidium and cesium solutes, we can offer no explanation. It looks like a transition from independent scatterer to interacting scatterer effects. On the other hand, the offset increases with increasing temperature, which is hard to understand. It would be valuable to verify the effect further.

### CONCLUSION

The Harrison suggestion accounts for the excess resistivity due to size effects fairly well in the case of alkali impurities in liquid sodium. The model predicts a linear increase for positive dilation and an almost exponential increase for negative dilation. This is incompatible with the use of Linde's rule with an effective valence change due to size. The comparison with experiment shows that the theory is probably as good as the data.

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I wish to thank E. Daniel for correspondence about this work, F. Sligh who carried out the experimental measurements, and S. Machlup for his suggestions about the manuscript.

### APPENDIX

#### Experimental Procedure

The sodium-potassium alloys were melted, mixed, and filtered in an all-stainless-steel system and pumped

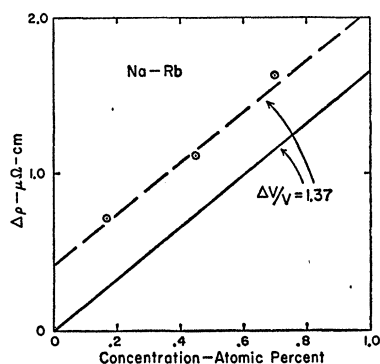


FIG. 4. Solute resistivity vs concentration for Na-Rb, 100°C. Data of reference 6. The dashed line has the predicted slope but is translated vertically to fit.

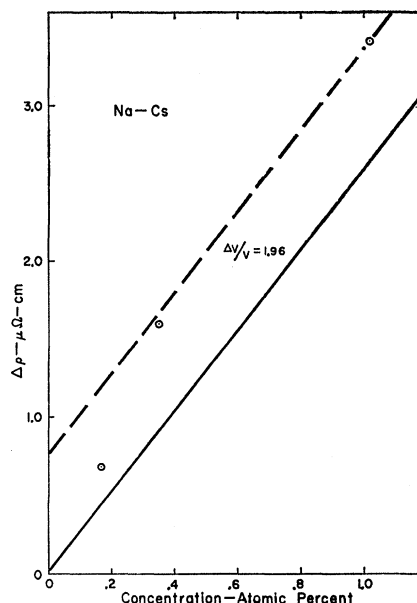


FIG. 5. Solute resistivity vs concentration for Na-Cs, 100°C. Data of reference 6. The dashed line has the predicted slope but is translated vertically to fit.

into glass sample holders. The holders were sealed off under argon at atmospheric pressure. Bubbles of gas adhered to the walls, but these were shaken loose while the samples were in the hot oil bath we used for temperature control, the temperature being held at 100°C.

The holders were previously calibrated by filling them with pure mercury. They are shaped like tuning forks with two tungsten electrodes at the tip of each leg. The resistances, of the order of 3 mohm, were measured by the potentiometer method. Chemical analyses were performed by the Analytical Laboratory of the Union Carbide Metals Company. Agreement was good between the analysis and that expected from the known weights of constituents.

The results are as follows:

Alloy	Resistivity ( $\mu\text{ohm-cm}$ )	Increase ( $\mu\text{ohm-cm}$ )
Na-...	9.77	...
Na-0.22 at.% K	9.94	$0.17 \pm 0.065$
Na-0.54 at.% K	10.30	$0.53 \pm 0.055$
Na-1.24 at.% K	10.97	$1.20 \pm 0.05$

These are averages of 10, 3, 5, and 6 measurements, respectively. The standard deviation of a single measurement is  $0.10 \mu\text{ohm-cm}$ . The error listed in the last column is one standard deviation.