

## Comments and Addenda

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### Thermoelectricity and Energy-Dependent Pseudopotentials

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In Li, the very low diffusion thermopower parameter ( $\xi \sim -8$ ) is indicative of strong scattering in the  $p$  wave, and an anomalously low result is to be expected for any method in which the scattering in one angular momentum component is stronger than that in any of the others. By contrast, when no one component dominates we obtain a substantially positive result (examples being Na, K, and Rb, for which  $\xi$  is in the neighborhood of  $+3$ ). The depressed value for Cs (0.2 in the solid,  $-1.3$  in the liquid) can be understood in terms of substantial (though, in the above sense, not quite dominant) scattering in the  $d$  wave. A standard phase-shift analysis of the electron-impurity scattering explains semiquantitatively the diffusion thermopowers of dilute alkali-alkali alloys, provided energy-dependent scattering data are used. Virtual recoil could provide desirable corrections.

IN recent contributions to the understanding of diffusion thermopowers in alkali metals<sup>1</sup> and their alloys,<sup>2</sup> the energy dependence of pseudopotentials was neglected, the approximation being necessary because the energy variations of the form factors<sup>3</sup> used were not available. If a pseudopotential were really local (i.e., a simple function of electron-ion separation), then the usual matrix element  $\langle \mathbf{k}' | v | \mathbf{k} \rangle$ , which in general depends on both  $\mathbf{k}$  and  $\mathbf{k}'$ , the incident and scattered wave indices, respectively, would reduce to a function of  $K = |\mathbf{k}' - \mathbf{k}|$  only. In other words, it would be characterized by the momentum transfer but not by the energy  $E = \hbar^2 k^2 / 2m$ . But, by their construction,<sup>3</sup> pseudopotentials are not local, so that their energy dependence becomes a matter for concern. As a result of experience with similar problems<sup>4,5</sup> in which energy-dependent data<sup>6</sup> were employed, we believe we can assess the effect of the  $k$  dependence.

<sup>1</sup> J. E. Robinson and J. D. Dow, *Phys. Rev.* **171**, 815 (1968), hereafter called RD.

<sup>2</sup> P. E. Nielsen and P. L. Taylor, *Phys. Rev. Letters* **21**, 893 (1968), hereafter called NT.

<sup>3</sup> A. O. E. Animalu and V. Heine, *Phil. Mag.* **12**, 1249 (1965), hereafter called AH. See also W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

<sup>4</sup> W. H. Young, A. Meyer, and G. E. Kilby, *Phys. Rev.* **160**, 482 (1967), hereafter called YMK.

<sup>5</sup> D. E. Thornton, W. H. Young, and A. Meyer, *Phys. Rev.* **166**, 746 (1968).

<sup>6</sup> A. Meyer, C. W. Nestor, and W. H. Young, *Proc. Phys. Soc. (London)* **92**, 446 (1967).

The full computational details and results are given in Refs. 4 and 5, and to these the interested reader is referred. However, in retrospect, it is clear to us that a number of the more important features (including those to be discussed below) depend less on the *precision* of the calculated data than on their *qualitative* character. For this reason, we place prime emphasis on the latter in the present article.

(i) *Pure metals.* Following earlier work<sup>7,8</sup> which suggested that the thermopowers of the solid alkalis might be understood by a proper inclusion of the lattice dynamics, RD obtained, after neglecting the energy dependence of their pseudopotentials, the results shown in Table I. There  $\xi$  is the usual parameter related to the thermopower  $S$  by  $S = -(\pi^2 k_B^2 T / 3 |e| E_F) \xi$ . In a note added in proof, they report a private communication from Bortolani and Calandra, who have calculated the  $k$  dependence of the AH potentials and found the corrections to  $\xi$  for Rb and Cs to be positive and very large, thus ruining the agreement with experiment in the former case and further aggravating the discrepancy in the latter.

We believe our work<sup>4</sup> on the corresponding liquids is relevant, since the experimental data (Table I) suggest

<sup>7</sup> J. E. Robinson, *Phys. Rev.* **161**, 533 (1967).

<sup>8</sup> J. M. Dickey, A. Meyer, and W. H. Young, *Proc. Phys. Soc. (London)* **92**, 460 (1967).

TABLE I. Thermopower data.\*

	$\xi$ (solid; room temp.)		$\xi$ (liquid; melting point)			$y$	$z$	
	Expt.	AH; no $k$ dependence	Expt.	AH; no $k$ dependence	YMK; $k$ dependence dropped	YMK; $k$ dependence retained	(liquid)	(liquid)
Li	-6.7	-3.5	-8.8	-8.0	-8.0	-5.3	4.1	3.2
Na	2.7	0.7	2.9	1.5	-1.0	0.4	2.4	-0.8
K	3.8	2.3	3.5	2.7	-2.4	1.5	2.8	-2.4
Rb	2.5	2.7	1.7	2.9	-4.0	0.5	3.3	-1.7
Cs	0.2	2.6	-1.3	2.9	-11.9	-4.9	4.1	2.8
Cu	-1.7		-3.5		-5.9	-3.4	3.1	1.4
Ag	-1.1		-1.9		-5.2	-3.2	3.0	0.6
Au	-1.5		-0.6		-6.6	-3.6	3.2	1.0

\* The theoretical solid-state  $\xi$ 's are RD's. Those for the liquids were computed by YMK using the mean structure factor suggested in Ref. 9; much the same over-all picture emerges when experimental structure factors are used (YMK Table V). The experimental data are taken from J. S. Dugdale, *Science* **134**, 77 (1961); the result of J. S. Dugdale and J. N. Mundy [*Phil. Mag.* **6**, 1463 (1961)] implies a value of  $\xi = -7.5$  for Li. The measured data for the liquids are taken from the review of N. E. Cusack, *Rept. Progr. Phys.* **26**, 361 (1963).

that the phase of a metal, be it liquid or solid, is not of crucial importance, at least in deciding the relative values of the  $\xi$ 's. Indeed, there is a good correlation between RD's average  $\xi$ 's and the equivalents<sup>4</sup> for the liquids (Table I) in which an isotropic structure factor<sup>9</sup> is used.

Apart from the allowance for the above difference in phase and the different scattering data<sup>6</sup> used, our procedure was the same as RD's, except that we calculated results with and without the energy dependence (Table I). Our qualitative conclusion, that the inclusion of  $k$  dependence very significantly increases  $\xi$ , is in agreement with the findings of Bortolani and Calandra, but in our case the effect was beneficial.

We were able<sup>4</sup> to write  $\xi = 2 - y - z$ , a form very useful for seeing the origin of our final results. To a first approximation,  $y$  reflects only the structure factor  $a(K)$ , and  $z$  only the electron-ion scattering. The following represents an improved analysis of these terms over that originally given. We take the terms in turn.

If  $a(K) \propto K^n$ , say, it follows *without approximation* [YMK Eq. (18)] that  $y = \frac{1}{2}n$ . In practice, the effective power varies from small values at low  $K$  to typically about 8 at  $2k_F$  for the monovalent metals.<sup>10</sup> The latter is all that usually matters, because of the heavy weighting at  $2k_F$ , so that  $y \approx 4$ . (See Table I; note that when scattering is significant in the lower- $K$  plasma<sup>11</sup> region,  $y$  is a little smaller because of a depressed effective power index  $n$ .)

The role of  $z$  is thus to explain departures of  $\xi$  from about  $-1$  or  $-2$ . We begin by noting the general relation  $\eta_l \propto k^{2l+1}$  (for low values of  $k$ ) for the phase shifts. Qualitatively (YMK Tables I and IV and, more explicitly, Fig. 4 of Meyer *et al.*), for  $l \neq 0$ , this relation is still good for  $k = k_F$ , but for  $s$  waves  $\eta_0$  is already de-

caying.<sup>12</sup> Thus, for  $k$  around  $k_F$ ,

$$\begin{aligned} k\partial\eta_0/\partial k &= \lambda\eta_0, \quad \lambda < 0 \\ k\partial\eta_l/\partial k &\approx (2l+1)\eta_l, \quad l \neq 0. \end{aligned} \quad (1)$$

Now, if a single  $l$  component is dominant, YMK Eq. (19) gives  $z \approx (\partial \ln \eta_l / \partial \ln k)_F \approx 2l+1$ ,  $l \neq 0$ . Such a situation corresponds to significant back scatter; the alternative limiting case throws emphasis on lower-angle scattering in which, qualitatively,  $s$ -wave behavior is decisive and a negative  $z$  is obtained. Examples of such behavior are Na, K, and Rb (Table I).

The origin of the anomalously low  $\xi$  for Li is now seen in the dominant  $p$  character which is evident in AH and in YMK [see Table I or Fig. 1(a) of the latter; remember it is enough that  $(2l+1)\eta_l$ , and not necessarily  $\eta_l$ , dominate]. Thus, here, we expect  $z \approx 3$ . Such a value is indeed obtained (Table I) and has been numerically checked (YMK Table V) to be insensitive to the structure factor used.

However, the YMK and AH data give very different results for Cs. YMK find enough  $d$ -wave dominance to make  $\xi$  strongly negative; the AH data correspond to mainly low-angle scattering (RD Fig. 4) with a  $\xi$  more akin to that of Na, K, and Rb. There is certainly strong  $d$  character not far above the Fermi level (which explains,<sup>8</sup> for example, the dramatic variation of the resistivity and  $\xi$  with pressure). Presumably YMK overestimate it and (as RD suggest) AH underestimate it. But the point emerges that increasing the  $d$ -wave scattering in the AH form factor and allowing for energy dependence should *lower*  $\xi$ . Thus the observed  $\xi$ , depressed below a typical positive plasma dominated value, is understandable, if rather tricky to compute accurately.

<sup>9</sup> N. W. Ashcroft and J. Lekner, *Phys. Rev.* **145**, 83 (1966).

<sup>10</sup> For polyvalent metals,  $n$  is negative near  $2k_F$  and the effect is to elevate  $\xi$ . This simply suggests why very few polyvalents (in contrast to monovalents) have negative  $\xi$ 's.

<sup>11</sup> J. M. Ziman, *Phil. Mag.* **6**, 1013 (1961).

<sup>12</sup> Qualitatively, these results seem to be model-independent. N. F. Mott and H. S. W. Massey [*The Theory of Atomic Collisions* (Clarendon Press, Oxford, 1965), 3rd ed., p. 33] show in the lowest parts of their Fig. 5 some scattering data for weak square wells. For electrons at the Fermi level and wells of the Wigner-Seitz radius, Mott and Massey's  $ka = 1.92$ .

Finally, in view of RD's speculation concerning the noble metals, we note that for these cases YMK obtain  $\xi$ 's of the correct sign because (a)  $y \approx 4$ , as explained above, and (b)  $z$  is small because [YMK Fig. 4(d)] there is about equal emphasis on back and plasma scattering.

(ii) *Dilute alloys.* NT propose a new mechanism—the virtual recoil of solute atoms—to explain the very-low-temperature thermopowers of certain dilute alloys of alkalis in alkalis. Their description involves (a) free-electron scattering from the perturbing potential of the impurity, (b) the (virtual) electron-phonon interaction, and (c) the neglect of the energy dependence of pseudopotentials. It is of interest, therefore, that a semiquantitative explanation is possible in terms of (a) without (b), provided the energy dependence of the pseudopotentials is kept.

Briefly, we make the qualitative point of the present approach, linking it to part (i) above. We begin with the result

$$\Delta\rho(k)/c = (12\pi^3\hbar N/e^2k^4) \sum l [\gamma_{l-1}(k) - \gamma_l(k)]^2, \quad (2)$$

which is either the usual impurity resistivity formula (in which the energy dependence is explicitly recognized) or the Ziman<sup>13</sup> modification of it, in an appropriate small-angle approximation. The  $\gamma$ 's are the phase shifts for the perturbing potential, which, at the Fermi level, satisfy the Friedel<sup>14</sup> rule

$$\sum (2l+1)\gamma_l(k_F) = 0. \quad (3)$$

They are related to the absolute  $\eta$ 's of MNY<sup>6</sup> by  $\gamma_l = \eta_l(\text{solute}) - \eta_l(\text{solvent})$ , both  $\eta$ 's being appropriate to the solvent  $k_F$ .

From (2) and the standard formula  $\Delta\xi = -\partial \ln \Delta\rho / \partial \ln E$ , we obtain

$$\Delta\xi(k) = 2 - \frac{1 \sum l (k\partial/\partial k) (\gamma_{l-1} - \gamma_l)^2}{2 \sum l (\gamma_{l-1} - \gamma_l)^2}. \quad (4)$$

[We use  $\Delta\xi$  where NT use  $\xi$  to distinguish from the parameter of part (i).] Positive  $\Delta\xi$ 's<sup>15</sup> occasion no surprise in view of the initial 2, but the negative values in the alkali alloys<sup>16</sup> require a special explanation via the second term.

Detailed examination of the fully quantitative calculations of Ref. 5 reveals that the following qualitative explanation operates in varying degrees in all cases. First, the scattering arising from the partial waves corresponding to  $l > 2$  is negligibly small. Second, of the remaining contributions, that for  $l=0$  is secondary, since its weighting is always small. This may be traced to (a) the  $(2l+1)$ -fold degeneracy associated with the  $l$ th partial wave [manifested through the coefficients  $l$  in

the sums in (4)] and (b) the further emphasis on the higher terms in the numerator of (4) through the energy gradient operator. To be more specific on the latter point, we note that (1) qualitatively describes both solute and solvent scattering<sup>6</sup> so that, near  $k_F$ , we may write

$$\begin{aligned} k\partial\gamma_0/\partial k &= \lambda\gamma_0, \\ k\partial\gamma_l/\partial k &\approx (2l+1)\gamma_l, \quad l \neq 0 \end{aligned} \quad (5)$$

where (Tables I and III of Ref. 5) the absolute value of  $\lambda$  never rises above 1.1.

To see how these effects lead to a negative  $\Delta\xi$ , it is illuminating, for illustrative purposes, to drop the  $s$  wave altogether, for then one can obtain a result from (3)–(5) without recourse to detailed calculations. From (3),  $\gamma_1(k_F) = 5\mu$  and  $\gamma_2(k_F) = -3\mu$ , say, where  $\mu$  is some constant. Then, from (5),  $(k\partial\gamma_1/\partial k)_F \approx 15\mu$  and  $(k\partial\gamma_2/\partial k)_F \approx -15\mu$ . Substitution of these values into (4) results in the cancellation of  $\mu$ , and one finds  $\Delta\xi(k_F) = -11/6$ . Basically, the mechanism requires a significant adjustment of charge between the  $p$  and  $d$  components around a substituted ion. Then, near  $k_F$ ,  $\gamma_1$  and  $\gamma_2$  are increasing rapidly (as third and fifth powers of  $k$ ) in absolute magnitudes, but with opposite sign because of the Friedel rule. Thus *both* the  $p$ - $d$  and  $d$ - $f$  (with  $f$  essentially absent) partial cross sections are growing rapidly with energy, the net effect being enough to make (2) also an increasing function of energy.

As has already been stated, the above picture is borne out semiquantitatively by the detailed calculations.<sup>5</sup> However, it should be remarked that in view of the remaining discrepancies between theory and experiment, there is room to accommodate the virtual recoil effect provided it were substantially smaller than NT estimate on the basis of the AH pseudopotentials.

Now, the pseudopotentials influence NT's results through a term  $\beta V_0$ . Here  $\beta$  is a complicated quantity [precisely but implicitly defined by Eq. (10) of the original article] but, by contrast,  $V_0$  is the forward-scattering matrix element (recall the terminology of the opening paragraph of this paper) for the perturbing potential and for electrons at the Fermi level and is simply and analytically characterized.<sup>3</sup> We thus find that if AH had used band masses appropriate to  $k = k_F$  instead of  $k=0$ ,<sup>17</sup> NT would have arrived at  $V_0$ 's which were significantly reduced in size and more in keeping with the viewpoint of the present work. However, while this is perhaps suggestive, it is far from conclusive, since (a) the term  $\beta$  would also change,  $\beta V_0$  being the physically meaningful quantity in this context, and (b)

<sup>13</sup> J. M. Ziman, *Advan. Phys.* **13**, 89 (1964).

<sup>14</sup> J. Friedel, *Phil. Mag.* **43**, 153 (1952).

<sup>15</sup> A. M. Guénault, *Phil. Mag.* **15**, 17 (1967).

<sup>16</sup> A. M. Guénault and D. K. C. MacDonald, *Proc. Roy. Soc. (London)* **A264**, 41 (1961); **A274**, 154 (1963).

<sup>17</sup> AH used effective masses appropriate to the  $k=0$  results of F. S. Ham, *Phys. Rev.* **128**, 82 (1962). This appears to have been accidental and certainly, for pure metals, the  $k=k_F$  values of Ham's second paper [F. S. Ham, *ibid.* **128**, 2524 (1962)] would have been more appropriate (see also RD's Ref. 33).

as with the work of Thornton *et al.*, the energy dependence should also, in principle, be incorporated. At the present time such a program would seem to be premature, since the corrections sought from virtual recoil would be smaller than the limits we can guarantee on the potential scattering results<sup>5</sup> because of the quantitative errors to which the calculated data are subject [cf. part (i)]. Also, as far as we are aware, no other

pseudopotentials have been calculated to date with this kind of accuracy.

A correspondence with Professor P. L. Taylor was most enlightening and is gratefully acknowledged. Some of this work took place in Sheffield during a visit by one of us (A.M.) made possible by grants from Northern Illinois University and the U. K. Science Research Council.

## Erratum

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**Possibility of Exciton Binding to Ionized Impurities in Semiconductors**, J.-M. LÉVY-LEBLOND [Phys. Rev. **178**, 1526 (1969)]. A line has been omitted between the 11th and the 12th line. The sentence should read "Sharma and Rodriguez claim that there is binding in the two separate regions  $\sigma \leq 0.20$  and  $\sigma \geq 4$ ."

In the second equation, instead of  $\langle \mathbf{P}_h^2/2m_h \rangle$ , read  $\langle \mathbf{P}_h^2/2m_e \rangle$ .

Reference 5 is now published: F. H. Gertler, H. B. Snodgrass, and L. Spruch, Phys. Rev. **172**, 110 (1968).

Finally, M. Rotenberg and J. Stein [Phys. Rev. (to be published)] have recently improved the estimate of  $\sigma_c$  and show that  $\sigma_c \simeq 0.454$ .