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The thermoelectric power of solid and liquid gadolinium

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Abstract. We have measured the thermopower, S , of pure Gd from about 300 °C to 1375 °C, well above the melting temperature of 1312 °C. Special care has been taken to remove H impurities from these samples. $S_{\text{solid}}(T)$ is similar to S for the light trivalent rare earths; evidence of a solid–solid phase transition is seen at about 1285 ± 10 °C. $S_{\text{liquid}} = -4.3 \pm 0.5 \mu\text{V } ^\circ\text{C}^{-1}$, and there is no apparent change in S across the melting temperature. S_{liquid} is compared with calculations via several theoretical models, including the new Bachelet–Hamann–Schluter pseudopotentials.

1. Introduction

For a variety of reasons, interest in the physical properties of the rare-earth (RE) metals has remained rather high. Steady but rather slow progress has been made in measurements of the electronic properties of the REs, especially at high temperatures and in the liquid. This is due in part to the high reactivity of these metals, and to the resulting difficulty in creating and maintaining sample purity. Measurements of electrical resistivity, ρ , have now been reported for nearly all of the liquid REs, and values of thermopower, S , are available for the light liquid REs and for the divalents, Eu and Yb (Van Zytveld 1989). These values of ρ show a nearly linear dependence on atomic number, Z , across the trivalent RE series, and values of S are also very consistent with one another. These imply that the electronic structures of the REs change little over much of the series. In this work, we report the first measurement of S on liquid gadolinium, for which special care has been taken to purify the sample material and to maintain that purity. This is then the first measurement of S on a purified heavy trivalent RE, and provides the opportunity to compare S for one of the heavy trivalent REs with S for the light members of this series. Also, because the REs fall into the class of strong-scattering metals, measurements of S provide an especially rigorous test of various theoretical models, and of their ability to properly describe these properties.

2. Sample materials and experimental methods

Pure Gd sample material was obtained from two sources: most samples were of 99.9% purity from AESAR/Johnson Matthey; one sample, of 99.5% from Atomergic Chemetals Corp., was measured in the solid only. Each sample was sealed by welding it into tantalum tubing under an argon atmosphere, and then was baked at high temperature under a vacuum of better than 10^{-4} Torr for about 3 d; this procedure removed hydrogen impurities that are

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normally resident in RE metals. Most samples were baked at a temperature about 50 °C above the melting temperature, T_{mp} ; no evidence of attack of the Gd on the Ta was seen. To be sure that even very small traces of Ta in the Gd would not affect our results, one sample was baked at about 50 °C below T_{mp} to further reduce the likelihood of contamination; measurements on this sample, in both the solid and the liquid, were indistinguishable from all others.

Containment of the liquid samples while measurements were being made proved to be difficult. Attempts were made to hold liquid Gd in Al_2O_3 and in BeO crucibles, but in each case evidence of progressive attack was seen, both in the measured results, and by visual examination of the crucibles after each experiment. BeO crucibles, coated with high-purity Y_2O_3 , proved to be more resistant to attack, but not adequately so. Initial results for liquid Gd held in Y_2O_3 (based on measurements made soon after melting, and before contamination was advanced) are fully consistent with the final results we do report here, however. There was no evidence of attack of *solid* Gd for any of the ceramic containers used; therefore, the extensive data we report on solid Gd were taken on samples that were removed from the Ta tubes in which they had been baked, and then were held in ceramic crucibles. Removing such samples from the Ta tubes permitted us to examine their quality: the wetting of the Ta by the liquid was excellent; the samples were bubble free, as anticipated, since they were stirred while liquid; and the surface meniscus did not exceed about 0.3 cm. Since we could find no ceramic to hold *liquid* Gd, the data we report for the liquid were all taken on samples held in sealed Ta tubes; because thermopower data measured in such a 'parallel conductors' arrangement are more susceptible to uncertainty, we normalized these data to those measured on the 'free' samples. (We will discuss this more fully below).

The liquid Gd samples held in Ta tubes varied in length from 5 cm to 10 cm. Pt-Pt 10% Rh thermocouples were spotwelded to these tubes at points 1.5 × the tube diameter or more from the ends of the Gd sample. We have determined that this placement reduces errors due to end effects to less than 1%. (See figure 1).

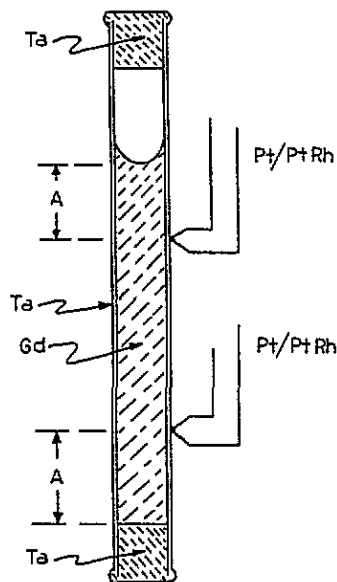


Figure 1. The physical arrangement for measurements of S for liquid Gd. Dimension A exceeded $1.5 \times$ the tube diameter to minimize end effects.

Thermal chromel wire was used as a counter-electrode material in measurements of thermopower, S , for the *solid* samples. This wire, as well as the chromel–alumel thermocouples used to measure the junction temperatures, was encased in 347 stainless-steel thin-walled tubing, and was further protected from the Gd sample by a thin Ta shoe to avoid reaction with the sample. These contacts were press-fitted into small holes drilled into the sides of the cylindrical Gd samples. The thermopower of the counter-electrode chromel wire was measured in our laboratory against pure copper, and is estimated to carry an uncertainty of $\pm 0.1 \mu\text{V } ^\circ\text{C}^{-1}$; the data from Roberts (1981) were used for $S(\text{Cu})$. Pt–Pt 10% Rh thermocouples and pure Pt counter-electrodes were used for the measurements on *liquid* Gd and on the very-high-temperature solid. These contacts were spotwelded onto the thin-wall Ta container. $S(\text{Pt})$ was taken from Roberts *et al* (1985).

As noted, measurements of S made on samples held in non-conducting containers carry an inherently smaller uncertainty. In particular,

$$S_x = S_s \pm dV/dT \quad (1)$$

where S_x is the sample thermopower, S_s is the thermopower of the counter-electrode material, and $V(T)$ is the measured thermoelectric voltage. $V(T)$ was obtained in each case by holding the temperature of one junction constant, typically to within $\pm 0.05 \text{ }^\circ\text{C}$, while ramping the temperature of the other junction. (The sign of the term dV/dT depends on the specific experimental arrangement used.) For samples held in conducting tubes, the cross-sectional areas of both the container (Ta, here) and of the sample, and the electrical resistivities of both the sample and container must be known at the temperature of interest, as well as S_{Ta} for the container. (The theory of the parallel thermocouple has been worked out by Wilson and Ulsh (1968). In this case

$$S_x = (1 + B)(S_s \pm dV/dT) - BS_{\text{Ta}} \quad (2)$$

where

$$B \equiv A_{\text{Ta}}\rho_x/A_x\rho_{\text{Ta}}. \quad (3)$$

Here, A_i is the cross-sectional area of the Ta container (Ta) or the sample (x), and ρ_i is the corresponding resistivity. It is clear that uncertainties in these parameters contribute to uncertainties in S_x . On the other hand, all of the additional parameters (except for S_{Ta}) can be drawn up into a single dimensionless parameter, B , as shown. In the present study, we take advantage of this by extending every high-temperature measurement on Gd from the liquid down to at least $50 \text{ }^\circ\text{C}$ below melting, and then adjusting B (≈ 0.6 here) slightly to normalize these data on solid Gd to the more reliable data taken on the ‘free’ Gd samples. (Note that B is also a (weak) function of temperature and ρ_x changes by a few percent across T_{mp} . These effects must therefore be included in the analysis.) Adjustments of B in this way for a given sample never resulted in an adjustment to S_x in excess of about $1 \mu\text{V } ^\circ\text{C}^{-1}$. In this analysis we have taken $\rho(\text{Gd})$ from Guntherodt *et al* (1974) and S_{Ta} from Vedernikov *et al* (1990). (It can be noted that generous estimates of variation and uncertainty in $\rho(\text{Gd})$ introduce uncertainties less than about $0.1 \mu\text{V } ^\circ\text{C}^{-1}$ in $S(\text{Gd})$.) We have also measured $S_{\text{Ta}}(T)$ in our laboratory against pure Cu, obtaining values that agree with those of Vedernikov *et al* to better than $0.5 \mu\text{V } ^\circ\text{C}^{-1}$.

We estimate that the accumulated total systemic errors introduced by this technique into our final values of S for liquid Gd do not exceed about $\pm 0.3 \mu\text{V } ^\circ\text{C}^{-1}$. In this way, we are able to reduce substantially the possible sources of error that are inherent in the parallel-conductors method.

3. Experimental results

The results of our measurements of $S(T)$ for several samples of Gd, both in the solid and in the liquid, are shown in figure 2. Earlier results due to Vedernikov *et al* (1977) and Burkov and Vedernikov (1985) are also shown. In the temperature range above 1250 °C, only representative data points are shown; many more measurements were made, and all of these were folded into the analysis. It is clear that $S(T)$ for solid Gd follows the general trend set by the light trivalent REs: S is relatively small in magnitude, varies slowly with T , and is concave downward with a maximum at a few hundred degrees Celsius. It also appears that there is a rather abrupt change in S at about $T_i = 1285 \pm 10^\circ\text{C}$; this is apparently associated with a solid–solid phase transition. It is interesting to note that this T_i is about 50 °C above a temperature, T'_i , that has been identified by some workers as a phase transition, but T_i is closer to the value (1255–1260 °C) at which Guntherodt *et al* (1974) see a change in a slope in their $\rho(T)$ data. In previous work on the light REs Pr, Nd and Sm, an increase in the measured solid–solid transition temperature has been associated with removal of H impurities (Kooistra *et al* 1988, Evele *et al* 1988, Beaudry and Gschneidner 1978). We attribute the higher transition temperature in our measurements to improved H purity as well.

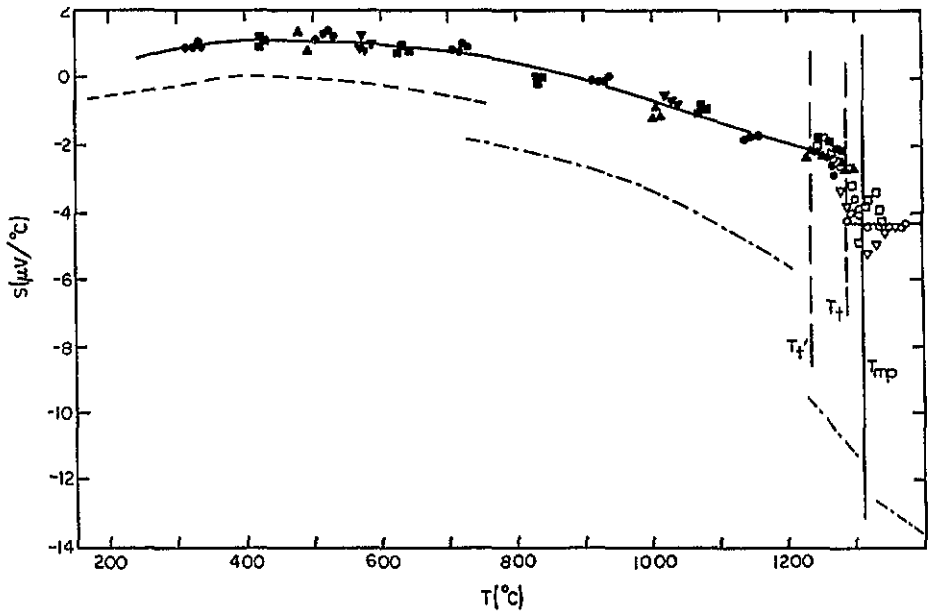


Figure 2. The measured thermopower, $S(T)$, for Gd. Present results: ∇ , \blacktriangle , \blacksquare , \bullet , 'free' samples resting in ceramic crucibles; ∇ , \square , \circ , samples contained in Ta. ---, Vedernikov *et al* (1977); - · -, Burkov and Vedernikov (1985).

We also note that no change in S across the melting temperature can be seen in our data. This is consistent with the results for the light trivalent REs. The only other measurement on liquid Gd that has been reported to date also shows only a small change across melting ($\sim 1 \mu\text{V } ^\circ\text{C}^{-1}$, Burkov and Vedernikov 1985). From our data, we obtain a value for S for liquid Gd of $-4.3 \pm 0.5 \mu\text{V } ^\circ\text{C}^{-1}$, where this includes the systematic uncertainties due to

the use of the parallel-conductors method for the liquid. (It should be noted that one single set of data in the liquid (see figure 2, open circles) spanned an unusually large temperature range. As a result, our smoothing procedure, which involved fitting a parabola to $V(T)$ via least squares, provided an especially stable result. These particular data points therefore should be among our best, and do occupy a position satisfyingly close to the centre of the distribution.)

There are some substantial differences between our data and those reported by Burkov and Vedernikov (1985); the differences between our data and those of Vedernikov *et al* (1977) in the common temperature range up to about 800 °C are much less, however. The former workers also found a discontinuity in $S(T)$ at approximately T_i' . These differences in S and in T_i are of the same type as, but of somewhat larger magnitude ($\times 2$) than, differences noted earlier between our measurements on Pr and Nd and those made by these authors. (See Kooistra *et al* 1988.) As before, we suspect that the differences are due to the special care we have taken to remove H impurities. (Vedernikov and coworkers also contained their samples in Ta, but did not bake these prior to making measurements on them.)

4. Discussion

The electrical resistivities, ρ , of the liquid trivalent REs show remarkable consistency with one another, varying nearly linearly with atomic number, Z , from La to Lu. The thermopowers of at least the liquid light trivalent REs (La \rightarrow Sm) are also rather similar, taking on values in the range from about -5 to $-9 \mu\text{V } ^\circ\text{C}^{-1}$ (Van Zytveld 1989). We now see from the present results that the thermopower of the first of the heavy trivalent REs, Gd, also falls very nearly into this range. It is quite apparent that, insofar as ρ and S sample the electronic character of these liquid metals, their electronic structures are very similar. The density of states near the Fermi level, which is reflected in ρ and in S , seems to be affected little by a substantial increase in the number of 4f electrons. (Steiner *et al* (1977), via XPS measurements, also find the valence band spectra of (solid) La and Gd to be nearly identical near E_F , with the filled 4f half-band (with seven electrons) in Gd shifted far below E_F .)

Some attempts have been made to calculate ρ and S for the liquid REs and for liquid Gd in particular. Waseda *et al* (1978) and Delley and Beck (1979a, b) have calculated values for ρ for several of the trivalent liquid REs, using the 'extended Ziman theory' developed by Evans and coworkers, and have obtained values that compare rather well with experimental values. Moreover, Delley and Beck (1979b), by including the sf-exchange interaction, were able to estimate a very small ($\sim 5\%$) magnetic scattering contribution to ρ for liquid Gd. This is in contrast to a very large room-temperature contribution, and is consistent with our results (that S is largely independent of Z) also. Delley *et al* (1978), from an analysis of resistivity data, suggest that the effective number of conduction electrons, n_{eff} , in the liquid trivalent REs is well below three increasing from about 0.5 to about 1.5 across the series. Waseda *et al* (1978) also calculate S for La, Ce and Gd on the same model. Their calculated values for S for liquid La and Ce fall rather close to the measured values, but their value for liquid Gd ($S = +3.35 \mu\text{V } ^\circ\text{C}^{-1}$) is rather far from the experimental value, and of the wrong sign.

Ballentine *et al* (1984) and Ballentine (1988) have used a different approach to calculate ρ and S for the liquid d and f metals. They use a linear combination of atomic orbitals (LCAO) method in combination with the Kubo-Greenwood formula to obtain expressions for ρ and S in terms of a 'diffusivity function'. This has some advantages over the extended Ziman

theory in that it does not assume the validity of the Boltzmann equation (of some question in strong-scattering systems), and it treats *s* and *d* states on an equal footing, permitting an estimate of the relative contributions of *ss*, *dd* and *sd* scattering to be estimated. While this method has not yet been applied to Gd, calculations for liquid La and Lu give a value of *S* that is negative and (at least for La) of the right magnitude. It would be very interesting to see the results of this calculation for liquid Gd.

Recently, Koubaa and Gasser (1990a–c) (KG hereafter) have used the first-principles energy-independent pseudopotential, $V_{\text{BHS}}(K)$, of Bachelet, Hamann and Schluter (1982) to calculate ρ and *S* for liquid Ga and Ge as well as for liquid GaGe alloys. (This pseudopotential has been used in many other applications, and is generally found to be very successful.) In this work they used the Ziman theory directly to calculate ρ and *S* but employed an approximation due to Heine, Abarenkov and Animalu to simplify V_{BHS} . Encouraged by the success of KG, we have used $V_{\text{BHS}}(K)$, obtained via the simplifying approximation of these workers, to calculate ρ and *S* for liquid Gd. However, in order to provide some guidance in these calculations, we first obtained ρ and *S* for liquid Gd using the empty-core-model potential of Ashcroft (1968) and the Lindhard dielectric screening function, with the experimental structure factor, $a(K)$, due to Waseda (1980). In this we took n_{eff} and R_c , the core radius in the model potential, as fitting parameters. Unique values of $n_{\text{eff}} = 1.60$ and $R_c = 0.844$ a.u. emerge from fitting these calculated values to the experimental values of ρ and *S* ($\rho_{\text{exp}} = 195 \mu\Omega \text{ cm}$). This value of R_c is reasonable, and $n_{\text{eff}} = 1.60$ falls interestingly close to the range of 0.5–1.5 suggested by Delley *et al* (1978). This screened potential, $V(K)$, is displayed in figure 3, and provides us with some guidance as we seek a more realistic pseudopotential via BHS.

Being guided by our initial calculations, we choose $n_{\text{eff}} = 1.60$ and calculate $V_{\text{BHS}}(K)$ using the approximation of KG: here this approximation means that the only angular-momentum component assumed to contribute significantly outside the core is that for $l = 2$. The screening function of Ichimaru and Utsumi (1981), $\epsilon_{\text{IU}}(K)$, is used, and we ignore spin-orbit effects, as do KG. We also display this screened potential in figure 3. A clearly non-realistic ρ ($> 1200 \mu\Omega \text{ cm}$) and a value of $S \sim +6.8 \mu\text{V } ^\circ\text{C}^{-1}$ results from using this potential in the Ziman formalism. (We use the experimental $a(K)$ throughout.)

We have therefore proceeded to calculate the full $V_{\text{BHS}}(K)$ including contributions from all of the various angular-momentum components, *l*, each weighted by the relative occupancy of that angular-momentum state by electrons outside the core for the atomic ground state. Spin-orbit effects were also included. The $V(r)$ obtained in this way was Fourier inverted and screened via the $\epsilon_{\text{IU}}(K)$, as well. This screened potential is also shown in figure 3. It can be seen that it more nearly approximates the fitted potential of Ashcroft, especially in the critical region near $2k_{\text{F}}$. Using this potential to calculate ρ and *S* provides $\rho = 585 \mu\Omega \text{ cm}$ (still about three times the experimental value) and $S = 8.7 \mu\text{V } ^\circ\text{C}^{-1}$. This is a considerable improvement, but is still rather far off the mark. Use of the (older) screening function, $\epsilon_{\text{VS}}(K)$, of Vashishta and Singwi (1972), provides values for ρ and *S* that are considerably worse. This screened $V(K)$ is displayed in figure 3, as well.

Finally, we increased n_{eff} to 3.0, and calculated $V(K)$ from the full BHS, screened by $\epsilon_{\text{IU}}(K)$. This potential, also displayed in figure 3, gives $\rho = 382 \mu\Omega \text{ cm}$ and $S = -13.6 \mu\text{V } ^\circ\text{C}^{-1}$. While this is considerably better for both ρ and *S*, we conclude that the first-principles model potential as presented by BHS, with a realistic value for n_{eff} , cannot be used in its present form with the Ziman formalism to calculate accurately the electron transport parameters, ρ and *S*, for liquid Gd. Bachelet *et al* (1982) do note that absolute errors in V_{BHS} are greatest for the 3*d* and 4*f* elements. An improved version of the model potential involving more parameters and including spin-polarization effects has

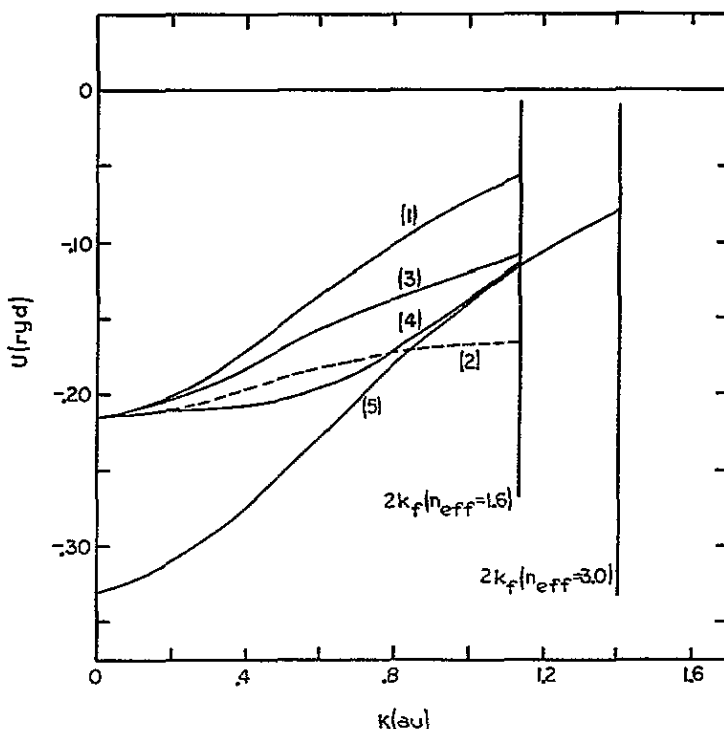


Figure 3. Model pseudopotentials used to calculate ρ and S for liquid Gd: (1) $V_{\text{Ash}}(K)$, $\varepsilon_{\text{Lind}}(K)$, $n_{\text{eff}} = 1.60$; (2) $V_{\text{KG}}(K)$, $\varepsilon_{\text{IU}}(K)$, $n_{\text{eff}} = 1.60$; (3) $V_{\text{BHS}}(K)$, $\varepsilon_{\text{IU}}(K)$, $n_{\text{eff}} = 1.60$; (4) $V_{\text{BHS}}(K)$, $\varepsilon_{\text{VS}}(K)$, $n_{\text{eff}} = 1.60$; (5) $V_{\text{BHS}}(K)$, $\varepsilon_{\text{IU}}(K)$, $n_{\text{eff}} = 3.00$.

been published for the 3d elements (Greenside and Schluter 1983), but no equivalent for the 4f elements has appeared to date. Perhaps, if and when such an improved potential is available, the transport properties of liquid Gd can be calculated more successfully. This and the method due to Ballentine appear to provide the best possibilities for such calculations at this time.

Acknowledgments

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