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HEAT CAPACITY AND THERMAL
DIFFUSIVITY OF ScD_x AND ErD_x

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HEAT CAPACITY AND THERMAL DIFFUSIVITY OF ScD_x AND ErD_x *

Marvin Moss
Thermophysical Properties

Abstract

The heat capacity, C_p ($T = 298$ - 1000 K), and the thermal diffusivity, α ($T = 623$ - 773 K), of ScD_x and ErD_x ($x = 0$ - 1.83) have been measured. C_p of ScD_x increases with x for $x = 0$ - 1.59 over the entire temperature range, but then declines for $x = 1.83$. ErD_x shows a monotonic increase of C_p with x , and exhibits a sharp positive anomaly at 910 K for $x = 1.82$. Both materials display an excess heat capacity which is attributed to disorder in the deuterium sublattice. A minimum in α is observed for ScD_x and ErD_x at mid-range values of x where disorder is greatest; α for all samples is fairly constant with T in this limited temperature range.

Introduction

The thermophysical properties of neutron tube target materials are among the important predictors of tube performance. Two candidate materials, ScD_x and ErD_x , have been measured in which x extends over the range of pure metal to the approximate upper limit of the two-phase (solution-dideuteride) region at room temperature. C_p was determined from 298 - 1000 K with a differential scanning calorimeter, and α was measured from 623 - 773 K by a ruby laser pulse method.

C_p anomalies were observed in both systems; an excess heat capacity, particularly large for intermediate x values, was noted and is attributed to disorder in the deuterium sublattice. Thermal conductivity, k , as a function of x parallels the room-temperature

electrical conductivity. This indicates that these materials remain substantially electronic thermal conductors as deuterium is added. The increase in k with x suggests a reduction in the electronic s-like character of the parent metal with less band-to-band electron scattering, at least to the maximum values of x examined here (≈ 2).

Experiment

Materials - All samples were prepared by the Neutron Devices Department, General Electric Company, St. Petersburg, FL. The scandium and erbium starting metals were 99.8% pure, minimum. A Sieverts loading system was used to enrich them with deuterium (99.56%, bal. hydrogen) to the following levels: ScD_x ; $x = 0, 0.50, 1.00, 1.31, 1.59, 1.83$, and ErD_x ; $x = 0, 0.50, 1.01, 1.31, 1.50, 1.82$. All values of $x > 0$ lie within the respective two-phase (solution-dideuteride) regions at room temperature; it is likely that the metal-deuterium phase diagrams for ScD_x and ErD_x closely resemble the corresponding metal-hydrogen diagrams.^{1,2} The structures of ScD_x and ErD_x for these values of x are alike; the solution phases are hcp and the dihydride phases fcc.

For $x < 2$, deuterium (or hydrogen) occupies the tetrahedral interstitial sites in preference to the octahedral sites of the hcp and fcc phases of both materials. Erbium forms a trihydride (trideuteride) but values of $x > 2$ for ScH_x (ScD_x) have not been observed.

Measurement

Heat Capacity - Heat capacity was measured with a Perkin-Elmer differential scanning calorimeter, Model DSC-2,

which has an upper limit of 1000 K. The samples were hermetically sealed in gold capsules with a cold-welding device, and the heat capacity measured relative to a pellet of sapphire similarly encapsulated. A measurement consisted in scanning a temperature interval from 5 K below to 5 K above the test temperature, at a rate of 10 K/min. This interval was sufficiently small as to avoid significant error arising from nonlinearity of C_p vs T. The DSC-2 was coupled to a data acquisition system which utilizes a Hewlett-Packard 2100S minicomputer.

The temperature range covered in these experiments was 298.1 to approximately 1000 K in intervals of 50 K. Intervals of 10 K were used for $\text{ErD}_{1.82}$ above 900 K. There was some initial concern about the loss of deuterium at high temperature through a possibly faulty seal in the capsule. Repeated measurements, however, yielded consistent results which indicated the integrity of all the seals. A related question concerns the amount of deuterium in equilibrium with the sample at high temperature in a perfectly sealed capsule. The $\text{ScD}_{1.83}$ sample at 1000 K represents the worst case of gas loss (highest vapor pressure) to the space within the container. The partial pressure of deuterium for this sample is approximately 1.3 kPa at 1000 K.² For a typical void space equal to 25% of the pellet volume, the ratio of deuterium in the space to that in the pellet is about 10^{-6} . This is too small a fraction to affect a measurement.

Measurements were randomized in that low and high test temperatures were mixed in a given series. This was done to preclude

instrument bias resulting from measurements being done in ascending or descending temperature cycles only. Results were repeatable provided that sufficient time was allowed (about ten minutes) for instrument and sample equilibration at each test temperature.

Thermal Diffusivity - Thermal diffusivity was measured by the flash technique developed by Parker et al,³ the basic ruby laser infrared detector system is described by Denman.⁴ The same samples were used for C_p and α measurements, the former being performed first. The diffusivity sample chamber was generally operated at pressures lower than 10^{-3} Torr which, in the 623-773 K experimental temperature range, resulted in no evident contamination of the unencapsulated samples nor loss of deuterium. It is anticipated that future measurements at higher temperatures will be performed on sealed samples with a thermocouple in contact with the back face.

Results and Discussion

Heat Capacity - Figures 1 and 2 show computer-derived curve fits to the C_p data for ScD_x and ErD_x , respectively. The experimental data are too numerous and overlap too much to be clearly portrayed graphically. Deviations of the data from the curves are generally a few percent. Table I gives the terms of polynomials representing these curves.

Figure 1 shows that deuterium increases the heat capacity of scandium, but the increase is not completely monotonic; the heat capacity of $ScD_{1.83}$ is less than that of $ScD_{1.59}$. For ErD_x , the increase of C_p with x is regular (Fig. 2) except at high

Table I. Computer-Derived Polynomials of C_p vs T for ScD_x and ErD_x

$$C_p = a_0 + a_1 (T - T_0) + a_2 (T - T_0)^2 + a_3 (T - T_0)^3 + a_4 (T - T_0)^4$$

		C_p in J/mole-K for T in K				
		x	a_0	$a_1 \times 10^2$	$a_2 \times 10^5$	$a_3 \times 10^8$
						$a_4 \times 10^{10}$
<u>ScD_x</u>		0	25.1	1.73	- 3.29	3.06
		0.50	32.0	2.60	- 0.0837	0.904
T=298.1-950 K		1.00	35.0	6.53	- 5.77	6.53
$T_0=298.1$ K		1.31	36.1	9.75	-11.5	9.54
		1.59	38.0	12.7	-18.2	13.2
		1.83	37.9	11.0	-15.3	11.5
		0	26.1	0.587	0.877	-3.97
<u>ErD_x</u>		0.50	32.5	5.90	-23.9	55.6
T=298.1-995 K		1.01	37.8	5.96	- 4.07	-4.03
$T_0=298.1$ K		1.31	40.4	9.95	-27.6	50.4
		1.50	42.6	10.3	-22.8	39.2
						-1.47
<u>ErD_x</u>						
T=298.1-910 K		1.82	46.6	6.79	13.2	-64.1
$T_0=298.1$ K						7.67
<u>ErD_x</u>						
T=910-990 K		1.82	98.1	-39.7	57.6	3,023
$T_0=910$ K						---

temperature; the curve for $ErD_{1.82}$ displays a sharp positive anomaly at 910 K. The experimental points for $ErD_{1.82}$ alone are shown

together with the computer fit in Figure 3. The anomaly, being as sharp as it is, cannot be assigned an accurate maximum value.

The several contributions to the heat capacity were analyzed. The heat capacity at constant pressure is given by

$$C_p = C_v^l + C_v^e + C^d + C^f \quad (1)$$

in which C_v^l and C_v^e are the lattice and electronic contributions to the heat capacity at constant volume, respectively.⁵ The dilation term, C^d , is equal to $AC_p^2\alpha$, A being a parameter which is experimentally found to be almost constant over a wide temperature range. C^f denotes any contribution to the heat capacity not accounted for by the terms described above.

The lattice term may be divided into two parts for materials like ScD_x and ErD_x ; one for the contribution of the metal atoms $C_v^l(M)$, and the other for the deuterium, $x C_v^l(D)$, $C_v^l(M)$ and $C_v^l(D)$ are molar quantities. The details of such an analysis are to be found elsewhere.⁶

When the first three terms on the right-hand side of Eq. (1) are accounted for, a quantity C^f remains (Figs. 4 and 5) which, at the higher temperatures, is much larger than the error in the analysis. The effect cannot be attributed to phase redistribution during the 10-K temperature rise of each measurement, since this would have produced a negative effect at one boundary of the phase diagram, grading to positive at the other. Actually, the effect was positive for all values of x and largest for the intermediate deuterium contents if the anomaly at 910 K for $\text{ErD}_{1.82}$ is not included.

A disorder model, originally applied to superionic conductors,⁷ was used to qualitatively explain the above results for ScD_x .⁶ A similar analysis for ErD_x seems plausible; the anomaly at 910 K for $\text{ErD}_{1.82}$ might even be explained this way.⁷

Extrapolation of the data of Figs. 1 and 2 to higher temperatures is difficult if one hopes to apply the model represented by Eq. (1). $C_V^{f(M)}$ is affected by lattice anharmonicities in an unpredictable way at high temperature. In addition, the magnitude of C^f is sufficiently great, with a quantitative model for it still lacking,⁶ that extrapolation is risky. For example, it is not known whether anomalies similar to the one for $\text{ErD}_{1.82}$ at 910 K will appear for $x < 1.82$ at higher temperatures (Fig. 2).

Thermal Diffusivity - The thermal diffusivities of ScD_x and ErD_x are shown in Figs. 6 and 7, respectively. The high-temperature data are more reliable; probable errors vary from an average of 15% at the lower temperatures to 8% at the high. Overall, α remains relatively constant in this restricted temperature range, and exhibits a minimum for mid-range values of x .

Thermal diffusivity, by definition, is

$$\alpha \equiv \frac{k}{\rho c_p} \quad (2)$$

where k is the thermal conductivity, ρ the density, and c_p the specific heat. (C_p , the heat capacity, represents the molar quantity, and c_p , the specific heat, the gram-mass quantity.) For k in W/cm-K, ρ in g/cc, and c_p in J/g-K, α will have the units of cm^2/s .

Values of ρ were determined by linear interpolation from data for bulk ScD_x and ErD_x representing high and low values of x . These are given in Table II; gram molecular weights, M , are also listed.

Table II. Densities and Gram Molecular Weights of ScD_x and ErD_x

	<u>x</u>	<u>$\rho(\text{g/cc})$</u>	<u>$M(\text{g})$</u>
<u>ScD_x</u>	0	2.983	44.956
	0.50	2.931	45.965
	1.00	2.951	46.963
	1.31	2.963	47.589
	1.59	2.974	48.161
	1.83	2.983	48.625
<u>ErD_x</u>	0	9.009	167.26
	0.50	8.880	168.27
	1.01	8.742	169.29
	1.31	8.662	169.90
	1.50	8.611	170.28
	1.82	8.525	170.93

The thermal conductivity, found from Eq. (2) is plotted in Figs. 8 and 9 for ScD_x and ErD_x , respectively. The errors in ρ and c_p being relatively small, the probable errors cited above for α apply to k . Since the high-temperature data are considered most reliable, k at 773 K was plotted against x for both materials (Fig. 10). After weak minima around $x = 0.5$, k rises rapidly with

x. The initial drop is probably due to increased electron scattering as deuterium dissolves in the metal.

Beyond the minima, the rise in k resembles the increase in the room-temperature electrical conductivity of several other hydrides.^{8,9} The thermal conductivity of scandium is largely due to electrons, the lattice contribution being small (3-10%).¹⁰ Between $x = 0$ and 2, the room-temperature electrical conductivity of ScD_x thin films increases by about a factor of 5; for ErD_x the factor is 3.¹¹ Application of the Wiedemann-Franz law relating electrical and thermal conductivities suggests that both materials remain essentially electronic thermal conductors as deuterium is added. The increase in electrical and thermal conductivities with x probably reflects the reduction in electronic s-like character of the metal as deuterium (or hydrogen) is added, with reduced band-to-band scattering.¹² This effect rapidly overcomes the scattering produced by the disordered state of the deuterium sublattice.

A projection of k beyond $x \approx 1.8$ should take into consideration the very rapid decline of the electrical conductivity of several hydrides.^{8,9,13} It remains to be seen whether k exhibits similar behavior.

Conclusions

The heat capacity and thermal diffusivity of ScD_x and ErD_x have been measured for $x = 0-1.83$ and $T = 298-1000$ K. C_p displays anomalously large values, a phenomenon which is attributed to disorder in the deuterium sublattice, particularly at mid-range

values of x . The thermal diffusivity (and thermal conductivity) is relatively constant with temperature in the range 623-773 K. The conductivity has a shallow minimum at low values of x , and then rises rapidly with x . The minimum is attributed to electron scattering in the disordered deuterium sublattice, and the rise to a reduction in band-to-band scattering.

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Figure 1. Heat capacity vs temperature for ScD_x ; computer-derived polynomial fits to data. See Table I.

Figure 2. Heat capacity vs temperature for ErD_x ; computer-derived polynomial fits to data. See Table I.

Figure 3. Heat capacity vs temperature for $\text{ErD}_{1.82}$; computer-derived polynomial fits to data. See Table I.

Figure 4. Excess heat capacity vs temperature for ScD_x . Measured C_p (Fig. 1) minus lattice, electronic, and dilational terms. See Eq. (1).

Figure 5. Excess heat capacity vs temperature for ErD_x . Measured C_p (Fig. 2) minus lattice, electronic, and dilational terms. See Eq. (1).

Figure 6. Thermal diffusivity vs temperature for ScD_x .

Figure 7. Thermal diffusivity vs temperature for ErD_x .

Figure 8. Thermal conductivity vs temperature for ScD_x.

Figure 9. Thermal conductivity vs temperature for ErD_x .

Figure 10. Thermal conductivity vs x for ScD_x and ErD_x at 773 K.