PHYSICAL REVIEW B VOLUME 16, NUMBER 10 15 NOVEMBER 1977

Schottky effect in Ag:Dy

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(Received 5 May 1976; revised manuscript received 3 December 1976)

Heat-capacity measurements on dilute dysprosium in silver yield a separation of 12 K between the ground and first crystal-field states of Dy^{3+}.

INTRODUCTION

Rare-earth metals diluted into cubic noble metals provide an interesting example for a violation of the simple rare-earth point-charge crystal-field model. The experimental findings of fourth-order terms with signs at variance with existing theory have been explained[1] via the hypothesis of a nonmagnetic 5*d* virtual bound state. The determination of the two crystal-field parameters for a given earth is rather difficult since the extreme dilutions required for complete homogeneity of the rare earth in the noble-metal matrix preclude the use of spectroscopic inelastic-neutron-scattering techniques. In the present paper, results are presented of heat-capacity measurements made on a silver-dysprosium alloy. From these measurements a determination of the splitting between the ground state and first-excited crystal-field state is obtained.

EXPERIMENTAL

The heat capacity was measured using an ac technique.[2] The sample was a single crystal chip[3] of silver weighing 13.2 mg, with about 325 ppm, or 40 nanomole, of ^{164}Dy. The output of a He-Ne laser was chopped at 10, 21, and 55 Hz and used to provide an ac heat input to the sample and to a Cu reference. ac and dc temperatures were measured with Cu-Au:0.07-at.%-Fe differential thermocouples relative to a Cu block heat sink with a calibrated Ge thermometer.

RESULTS

The measured specific heat after addenda corrections is shown in Fig. 1(a), plotted as C/T vs T^2, for temperatures from 1.6 K to about 10 K. The solid line corresponds to pure Ag, as measured in a separate experiment. Other data to 15 K, not presented here, are consistent with the pure Ag values within experimental error.

The data were least-squares fit from 1.6 to 10 K to a theoretical curve. The equation for the specific heat is

$$C/T = \gamma + \beta T^2 + \alpha T^6 + C_S/T,$$

with C_S the Schottky term

$$C_S = (Nk/T^2)(\langle E^2\rangle - \langle E\rangle^2),$$

where N is the number of Dy^{3+} ions and the angular brackets denote thermal averages over the degenerate crystal-field energy levels expressed in temperature units. The crystal-field levels are distributed according to the Hamiltonian

$$H = B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4),$$

where the quantities in parentheses are the standard operators, and $B_n = V_n \theta_n$, where θ_n is the reduced-matrix elements. The quantities γ and β are the conduction electron and first-order lattice coefficients. The term in α involves a correction for higher-order lattice contributions. Assuming α is 10^{-6} mJ/mole K^8, the correction for pure Ag amounts[4] to about 5% at 10 K and essentially zero at 5 K. The previous measurements on Ag then agree with the simple formulation to within a few tenths of a percent over the range 1.6–10 K. Since the present raw data exhibit about 3% scatter, the parameter α was fixed in the fits.

Previous ESR and magnetic susceptibility data[1,5,6] had indicated a Γ_7 ground state with a Γ_8 first excited state lying fairly close. Thus the present calculations involved searching the region of crystal-field parameters, V_4 and V_6, which would satisfy these requirements. An original work[1] indicated a ground state isolation of only 1 K; the later ESR work indicated[6] 11.5 (1.0) K. The current data provide a good indication of the initial (low-temperature) slope of the Schottky peak. Calculations indicate that the second excited Dy^{3+} level does not contribute substantially to this slope for any value of the ratio of sixth- to fourth-order parameters x (in the terminology of Lea, Leask, and Wolf[7]) for x satisfying $0 < x < 0.6$. Thus, the position of the first-excited state can be uniquely de-

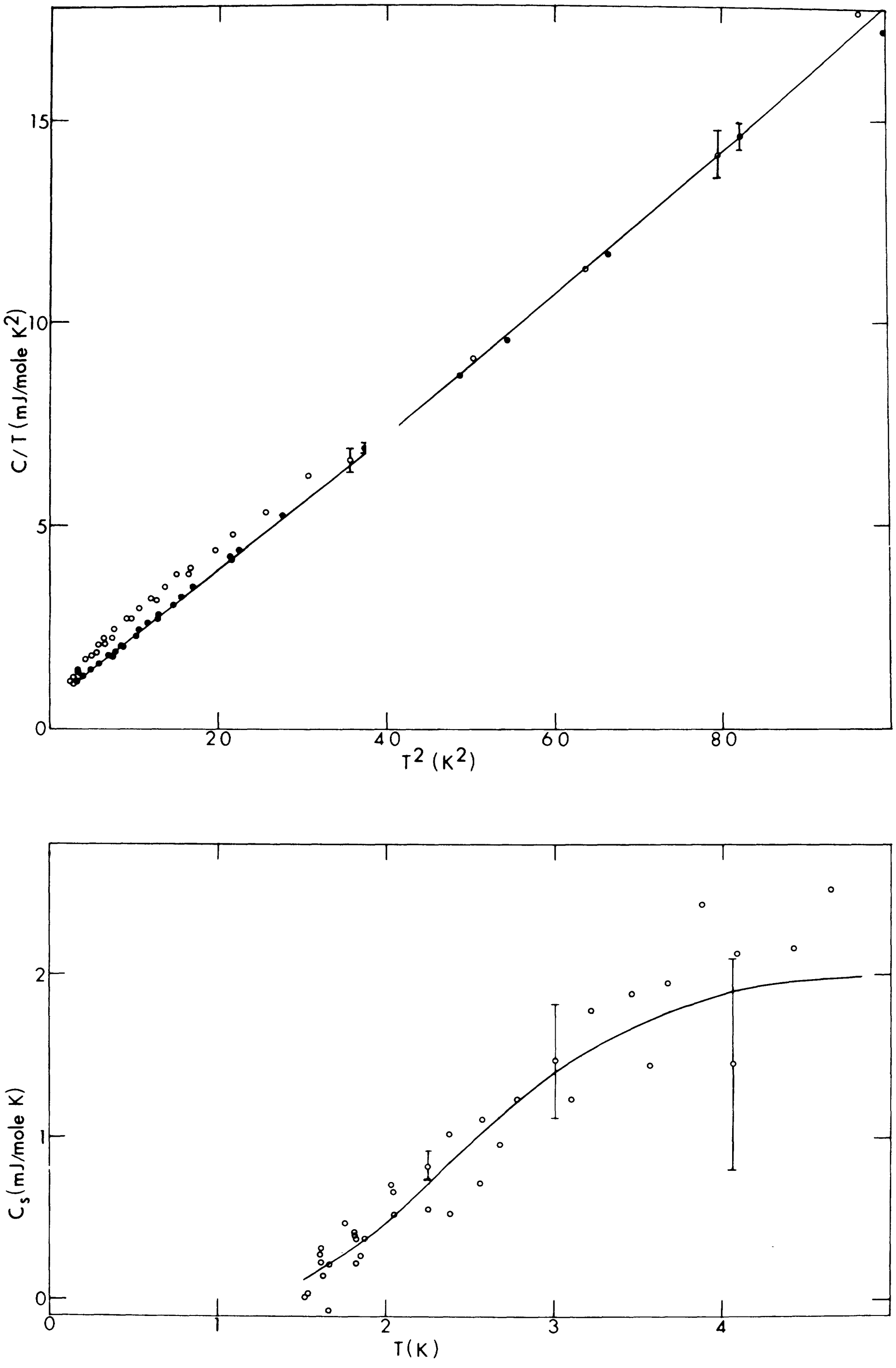

FIG. 1. (a) Heat capacity of Ag:Dy (325 ppm) from 1.6 to 10 K plotted as C/T (open symbols) per mole Ag. The solid line corresponds to the separately measured heat capacity of Ag (filled symbols). (b) Ionic heat capacity C_S of Dy^{3+} in Ag:Dy per mole Ag after subtraction of the fitted lattice and conduction-electron contributions (open symbols). The solid line corresponds to a ground-state isolation of 11.7 K.

termined.

The parameters obtained from the fit are given in Table I. The Schottky specific heat is shown in Fig. 1(b). This fit assumes a three level sequence, doublet-quartet-quartet, with relative energies 0:1:3. A two level sequence increases Δ (energy separation between ground and first excited states) by 0.1 K, a change much less than the 1-K statistical error. Diagonalization of the Hamiltonian indicates the smallest relative separation of the levels at $x = 0.36$ with a sequence spacing 0:1:1.9. Fitting with this constraint, Δ decreases by 0.9 K.

TABLE I. Specific-heat parameters in Ag:Dy. Δ is the separation between ground state and first-excited state. Units are per mole Ag. Errors in parentheses are statistical errors only.

Schottky height (mJ/mole K)	Δ (K)	γ (mJ/mole K^2)	β (mJ/mole K^5)
2.5(4)	11.7(1.0)	0.74(5)	0.161(4)

The change is, again, less than the error and the quality of the fit is slightly worse.

The Schottky height parameter is 2.5 (4) mJ/mole K (moles Ag) or 0.9 (2) times the expected 2.70 mJ/mole K. The electronic coefficient is 0.74 (5) mJ/mole K^2. Other reported values range[4,8] from 0.61 to 0.68. Experiments[8] indicate γ should increase by an amount proportional to the incremental electron per atom ratio, an immeasurably small change in this case. Agreement with the reported values is fairly good, considering the unexplainable variations. The lattice term $\beta = 0.161$ (4) (or a Debye temperature of 229 K), agrees well with the tabulated 0.167 (4) and should be little affected by the small amount of Dy in the sample.

The ground-state isolation of 11.7 K obtained in this work agrees with the 11.5 K determined in the ESR measurements.[6] Unfortunately, it is impossible to singularly determine the fourth- and sixth-order crystal-field parameters from the isolated Schottky peak. At temperatures higher than about 10 K, theoretical specific-heat curves differ significantly for various values of x. Data in this region of temperature would, therefore, be sufficient to determine both V_4 and V_6. On the assumption of a first excited level at 12 K, calculations show a linear relationship between V_6 and V_4 over a wide range of V_4:

$$V_6 = -0.18V_4 + 0.3 \text{ (meV)}.$$

Taking $V_4 = -6.0$ meV as estimated in Ag:Er,[1] then $V_6 = 1.4$ meV for Ag:Dy. This compares with 1.1 meV in Ag:Er. An overall crystal-field splitting is estimated at a reasonable 150 K, and $x = 0.52$; this compares well with $x = 0.54$ obtained in the previous study.[6]

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*Work supported by the NSF.

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