film should appear more important than the details of the lattice or cluster statistics. Watson and Leath[7] gave an exponent of 1.38 for a simple 2D site system, tending to confirm that the critical exponent would not depend strongly on the type of lattices. This appears in favor of our result.

In summary, we have measured the electrical conductivity of an ultrathin film and applied a novel test for percolative conduction. The results were interesting and rather in conformity with the 2D continuum percolation model.

The authors wish to thank Professor Y. C. Lee, Professor F. Y. Wu, and Professor E. N. Foo for their useful and stimulating discussions.

*Work supported by the National Science Council of the Republic of China.

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Pressure Dependence of the Magnetic Properties of Mixed-Valence TmSe

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(Received 26 April 1976)

Measurements of the magnetic moment of TmSe show that the low-field susceptibility and the multiboundary field-temperature (H_0-T) phase diagram at low temperatures depend strongly on hydrostatic pressure. For $\vec{H}_0 \| [100]$ the upper transition fields increase at a rate $\simeq +1.7$ kG/kbar. The magnetic properties reflect the valence changes of Tm^{2+} to Tm^{3+} as the lattice contracts, and for $P \gtrsim 20$ kbar, the Tm ion should be trivalent.

In this Letter we report the first observations of the hydrostatic pressure dependence of the multiboundary phase diagram[1] of TmSe, a material reported to show mixing of the Tm^{2+} and Tm^{3+} states.[1-4] Much of the experimental and theoretical work in mixed-valence systems[4] has involved the Sm monochalcogenides which undergo a semiconductor-to-metal transition and become mixed valent at high hydrostatic pressures. However, TmSe exhibits some mixed-valence characteristics at atmospheric pressure, and has several field-dependent magnetic anomalies at low temperatures. In the present work the phase diagram associated with these anomalies was determined by measurements of the magnetic moment, σ, as a function of temperature ($1.4 \leq T \leq 21$ K), applied field ($0 \leq H_0 \leq 60$ kG), and hydrostatic pressure ($0 \leq P \leq 10.4$ kbar). The phase boundaries in the H_0-T plane for TmSe change rapidly with pressure; with $\vec{H}_0$ parallel to the [100] direction, the higher-field transitions increase at a rate of $\simeq 1.7$ kG/kbar. The pressure dependence of the low-field susceptibility at 4.2 K is an order of magnitude larger than previously observed for singlet-ground-state rare earth monochalcogenides and monopnictides.[5] The magnetic properties reflect the valence changes of Tm as a function of H_0, P, and T. The large

changes of the phase diagram with pressure are consistent with the conversion of Tm^{2+} to Tm^{3+} as the lattice contracts. Both the magnetic data and independent arguments based on the relation between valence and lattice constant show that for $P \gtrsim 20$ kbar the Tm ions should be trivalent in TmSe.

The single-crystal TmSe sample used in our experiments was obtained from M. Campagna and was part of the same sample[6] used earlier.[1,3] The sample was placed in a small high-purity (cobalt-free) beryllium-copper clamp device producing hydrostatic pressures up to $\simeq 10$ kbar. The entire clamp-plus-sample assembly was attached to a vibrating-sample magnetometer; the applied magnetic field was generated by a 60-kG high-homogeneity superconducting solenoid. The background moment of the clamp was negligible compared to that of the sample reported here. Details of the experimental procedure are described elsewhere.[7]

The pressure dependence of σ versus H_0 at $T = 1.4$ K is illustrated in Fig. 1(a). The general features are these: (1) H_T [where H_T is the field for the maximum of $(d\sigma/dH_0)_{P,T}$ determined by numerical differentiation] increases as P increases; (2) the change in σ at H_T decreases as P increases; (3) as P increases the low-field susceptibility decreases and approaches a constant value; (4) for all P, the high-field ($H > H_T$) characteristics of σ are similar. The low-field slope of σ versus H_0 for $P \gtrsim 8$ kbar intersects the high-field magnetic moment data at $H_0 \simeq 41$ kG ($\sigma \simeq 45$ emu/g). In Fig. 1(b) we plot H_T versus P for six pressurizations. The dashed line is an extension of the line drawn between the values of H_T at $P = 0$ and $P = 4.0$ kbar and intersects 41 kG at $P = 18$ kbar (see arrow). The slight, but systematic, departure of the data from the dashed line of Fig. 1(b) suggests that $P = 18$ kbar is a lower limit at which the step in σ versus H_0 of Fig. 1(a) is expected to disappear.

The phase diagram of TmSe determined from our data is shown in Fig. 2. The various phase boundaries for $P = 0$ are labelled I to IV, following Ref. 1. The transition at phase boundary III is seen clearly as the step in σ versus H_0 of Fig. 1(a). The transition associated with II is not visible on the scale of Fig. 1(a). (This transition also shows hysteresis with H_0.) Our data for $P = 0$ are in good agreement with those of Ref. 1. The general effect of pressure is to *increase* H_T at a rate $dH_T/dP \simeq 1.7$ kG/kbar for $\vec{H}$ along the [100] direction.

It is difficult to explain the multiboundary phase diagram of TmSe by means of *simple* long-range

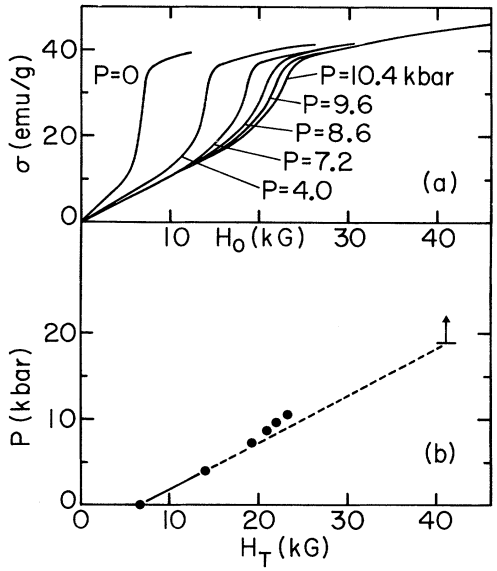

FIG. 1. (a) Magnetic moment σ versus H_0 of TmSe [100] for six pressurizations at $T = 1.4$ K; (b) P versus H_T derived from (a). H_T is the field for the maximum of $(d\sigma/dH_0)_{P,T}$ determined the numerical differentiation. The dashed line, an extension of the line between values of H_T at $P = 0$ and $P = 4.0$ kbar, defines a lower limit for pressure (indicated by the arrow at $P \gtrsim 18$ kbar) at which the step in σ versus H_0 is expected to disappear.

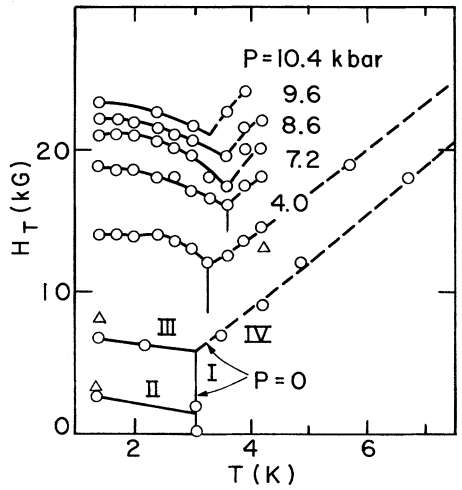

FIG. 2. H_T versus T phase diagram of TmSe [100] for six pressurizations. Circles are data obtained with $\vec{H}_0 \| [100]$, and triangles are for $\vec{H}_0$ at an angle to [100]. Roman numerals I to IV label the phase boundaries at $P = 0$, using the notation of Ref. 1. Boundaries IV for $P = 0$ and $P = 4$ kbar are linear up to $T = 16$ and 12K, respectively. For higher T the transition fields are difficult to define.

ordered antiferromagnetic structures. First, no evidence for long-range magnetic order has been obtained by neutron scattering.[8] Second, we conclude that the $P=0$ phase diagram in Fig. 2 is not consistent with the expected phase boundaries for a simple antiferromagnet, or for a simple metamagnet. For a spin-flop transition to occur at H_{sf}, the susceptibility below H_{sf} must be smaller than that above H_{sf}. The data in Fig. 1 do not satisfy this criterion at boundaries II or III. If we assume a simple *metamagnetic* structure below 3 K, and if boundary III involves a metamagnetic transition, its T dependence is reasonable, but boundary IV is still difficult to explain.[9] Various short-range order models or more complex long-range order models may be applicable to TmSe, but we defer discussion until more definitive evidence for such ordering is available.

The relation between the *ionic volume* and the *valence* of Tm may be used to describe the effects of hydrostatic pressure on TmSe. On the basis of x-ray data for TmSe (see Fig. 3 of Ref. 2), increasing P favors Tm^{3+} because the ionic volume is reduced.[10] Recent magnetostriction measurements to high fields[11] show that the volume *increases* ($\Delta V/V \simeq 4\times 10^{-4}$) as the field increases across boundary III or IV. Thus, increasing H_0 favors Tm^{2+}, but the volume expands only slightly with H_0. The competing effects of P and H_0 are illustrated in Fig. 1(a): (1) As P increases, the initial susceptibility decreases, consistent with an increased Tm^{3+} contribution (we expect $\chi^{3+} < \chi^{2+}$ at low T); (2) the smaller change in σ at H_T for higher P reflects the smaller contribution of the remaining Tm^{2+}; (3) the slow approach to saturation of σ versus H_0 at high fields (above H_T) is characteristic of crystal-field splittings of the ground states of Tm^{2+} and/or Tm^{3+}.

Extrapolation of the x-ray data (Fig. 3 of Ref. 2) indicates that a reduction in volume of ~4% for TmSe would completely convert it to $Tm^{3+}Se$. Based on estimates of the compressibility,[5,12] a pressure of 10 kbar leads to $\Delta V/V \sim 2\%$, which is 50% of that needed for complete conversion to $Tm^{3+}Se$. Thus the magnetic properties at our highest pressure (10.4 kbar) should reflect a substantial increase of Tm^{3+} concentration consistent with observations. Furthermore, $P \gtrsim 20$ kbar should lead to nearly complete elimination of Tm^{2+} as well as any valence fluctuations. It should be noted that the above argument is independent of our magnetic data, but is consistent with the results of Fig. 1, which show that for $P \gtrsim 18$ kbar the step in σ versus H_0 is expected to disappear.

If the phase boundaries of TmSe are not associated with long-range magnetic order, an alternative description for the observed transition at boundaries III and IV may involve field-induced valence changes. Based on the small volume changes observed at boundaries III and IV, we conclude that only a small change in Tm^{3+}-Tm^{2+} concentration occurs there. Complete transformation from Tm^{2+} to Tm^{3+} (or the inverse) would imply a volume change which is orders of magnitude larger than that observed. A field-induced reduction of the valence mixing is consistent with the small volume changes observed at III and IV. In this case the increase in σ versus H_0 may be associated with the $Tm^{2+}Se$ component, which should have a magnetic crystal-field ground state.

We have shown that for TmSe the magnetic properties and the large changes of the phase diagram with pressure are consistent with conversion of Tm^{2+} to Tm^{3+} as the lattice contracts. The magnetic data, and independent estimates based on the relation between valence and lattice constants, show that for $P \geq 20$ kbar, the Tm ions should be trivalent in TmSe. It should be emphasized that before detailed models are considered to describe the properties of TmSe, it is necessary to repeat measurements of the microscopic properties of TmSe in properly chosen materials. For example, long-range order has not been observed for TmSe with neutron scattering,[8] but the re-examination as a function of H_0 is warranted at $T < 3$ K using a TmSe sample for which the multiboundary phase diagram is observed. Finally, various experiments at $P \geq 20$ kbar should show the properties of trivalent TmSe.

We are grateful to M. Campagna and L. D. Longinotti of Bell Laboratories for furnishing the TmSe samples. We wish to thank Y. Shapira for measuring the magnetostriction to high fields and for several valuable discussions and E. J. McNiff, Jr., for measuring the magnetic moment to 150 kG. We wish also to thank M. Campagna, E. Bucher, H. R. Ott, K. Andres, W. M. Walsh, Jr., R. D. Parks, C. Goncalves da Silva, and C. Varma for informative discussions.

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*Work supported by National Science Foundation Grant No. DMR 75-09494. Visiting Scientist at the Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Mass. 02139.

†On leave from Universidade de São Paulo, São Paulo, Brazil. Work supported by Fundação de Amparo á Pes-

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