(1976); M. R. Halse and J. C. Taunton, in *SQUID*, edited by H. D. Hahlbohm and H. Lübbig (W. de Gruyter, Berlin, New York, 1977), p. 71.

[3]U. K. Poulsen, Rev. Phys. Appl. 9, 41 (1974); R. E. Harris, Phys. Rev. B 10, 84 (1974).

[4]B. S. Deaver, R. G. Boone, and R. Rifkin, Phys. Lett. 57A, 186 (1976); H. Højgaard Jensen and P. E. Lindelof, J. Low Temp. Phys. 23, 469 (1976); Kazuo Hida and Yoshiyuki Ono, private communication.

[5]N. F. Pedersen, O. H. Soerensen, and J. Mygind, to be published.

[6]O. H. Soerensen, J. Mygind, N. F. Pedersen, V. N. Gubankov, M. T. Levinsen, and P. E. Lindelof, to be published.

[7]I_c was measured by recording about 100 I-V curves on a storage oscilloscope. We identified the largest value recorded with the critical current. The reproducibility of the procedure was better than 0.1% and comparable to the long-term stability of the He-bath temperature.

[8]A resonant response was also observed using scheme A. Because of the low Q of the plasma resonance in our junctions, this resonance ($f_p = 2f_1$) overlapped strongly with the wing of the $f_p = f_1$ resonance and was not clearly resolved.

[9]The Q may include surface losses in the superconducting films and may depend on the applied microwave power level. No estimate is attempted.

[10]The capacity depends only on geometry and barrier properties which are assumed independent of temperature in the narrow temperature range of the experiment.

Field-Dependent Magnetic Phase Transitions in Mixed-Valent TmSe

H. Bjerrum Møller[a] and S. M. Shapiro
Brookhaven National Laboratory, Upton, New York 11973

and

R. J. Birgeneau
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 11 August 1977)

A neutron diffraction study of the field-dependent magnetic ordering in TmSe is reported. The magnetic strucutre in zero field is antiferromagnetic fcc type I with $T_N = 3.2$ K. The magnetic phase diagram may be understood as a successive domain reorientation and metamagnetic transitions for $T < 3$ K with increasing field. We can explain this quantitatively using a simple classical spin Hamiltonian. The mixed-valent character manifests itself mainly in a reduced moment and in a markedly altered crystal field.

The magnetic properties of rare-earth mixed-valent compounds have been a subject of controversy for a number of years.[1,2] Until recently, it was generally believed that conventional magnetic ordering was not possible in mixed-valence materials if the fluctuation energy was large compared with the exchange energy. Varma,[1] however, has predicted that long-range magnetic order be possible provided that both rare-earth valence states are magnetic. The best-known example in which this situation is achieved is the rock-salt chalcogenide TmSe.[3] Early unpublished neutron diffraction experiments by Cox *et al.*[3] in a polycrystalline sample of TmSe indicated complex magnetic correlations but no true long-range order at 1 K. However, more recent macroscopic measurements,[4-8] including susceptibility, thermal expansion, elastic constants, and magnetostriction, on well-characterized single crystals indicate a well-defined phase transition at $T \simeq 3$ K. The magnetic-field dependence of the ordered state appears to be quite anomalous.[5-8] The nature of this magnetic state and its relationship to the mixed-valence fluctuations remains mysterious.

In order to clarify the magnetism of TmSe we have carried out a neutron diffraction study of the magnetic ordering on a well-characterized single crystal[9] of TmSe. We demonstrate that conventional long-range order is indeed achieved ($T_N = 3.2$ K in our sample) thus giving unambiguous configuration of Varma's prediction. The ordering is fcc type I antiferromagnetic (a/f). We show that in a magnetic field there is only one bona-fide phase boundary separating the a/f phase from the paramagnetic (para) phase. The magnetic properties of TmSe may, in fact, be simply understood using a classical spin Hamiltonian. The principal manifestations of mixed-valent effects seem to be a drastically altered

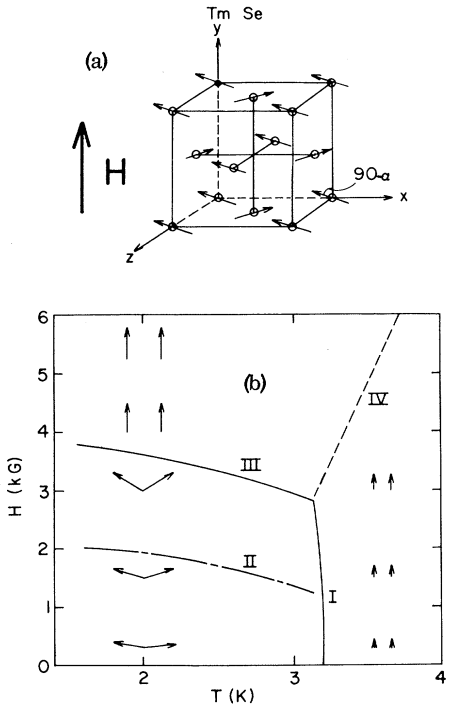

FIG. 1. (a) Magnetic structure of monodomain TmSe for a field along the (010) direction. The tetragonal axis is along the z direction. A modest magnetic field turns all of the spins through the angle α out of their positions along (100) in zero field. (b) Magnetic phase diagram of TmSe with the magnetic field applied in the (100) direction.

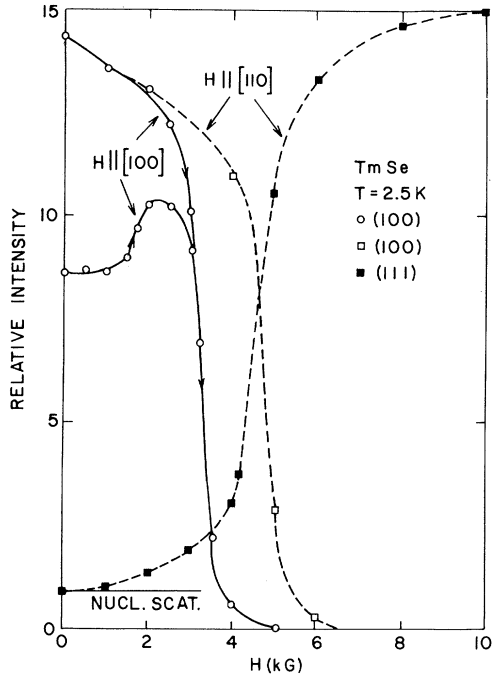

FIG. 2. Relative intensity of Bragg reflections vs applied magnetic field at $T = 2.75$ K.

magnetic anisotropy and a reduced Tm moment.

The experiments were carried out on a two-axis spectrometer at the Brookhaven National Laboratory high-flux–beam reactor using conventional neutron diffraction techniques. A "good" sample with well-defined phase transitions was kindly supplied by Walsh *et al.*[9] Resistivity and susceptibility measurements on adjacent pieces indicated a sharp well-defined transition at ~3 K. The crystal, which had a mosaicity of 0.3 deg, was a platelet $5\times3\times1$ mm^3. The lattice parameter was 5.71 Å at room temperature; using conventional linear-interpolation techniques,[4] this lattice constant implies a mixed valence of about 80% $Tm^{3+}(4f^{12})$ and 20% $Tm^{2+}(4f^{13})$.

We consider first the results in zero field. Below 3.2 K magnetic Bragg scattering appears at all of the forbidden fcc positions (h,k,l), that is, with h, k, and l integers but neither all even nor all odd. This is immediately suggestive of a multidomain sample with type-I a/f order. This is a tetragonal magnetic structure with planes perpendicular to one of the cube axes. As illustrated in Fig. 1 the magnetic moments are parallel within the planes but oppositely directed in successive neighboring planes. From the observed magnetic scattering, we find that the relative intensities of the sixteen magnetic superlattice reflections studied are accurately reproduced, assuming *a/f type-I structure with the spins pointing along (100) directions perpendicular to the tetragonal axis* and assuming equipopulation of the six possible domains. The magnetic form factor, also obtained from these measurements, is in close accord with the theoretical form factor for Tm^{3+}. This by itself is a surprising result which warrants further investigation. Finally, by normalization of the magnetic intensities to the weak nuclear reflections we deduce an ordered a/f moment of $(1.7\pm0.2)\mu_B$. As we shall discuss later, both the spin direction and the small moment are anomalous.

An unusual phase diagram with some rather exotic explanations has been observed in TmSe under application of a magnetic field.[5-8] We find a similar phase diagram (Fig. 1) for $\vec{H}$ along [100] as determined from the magnetic intensities shown in Fig. 2. However, a straightforward simple picture emerges from our direct observations of the magnetic order. No measurable change in

lattice parameter was observed at any of the phase boundaries. This eliminates any possibility of a mixed-valence phase transition. At phase boundary I (Fig. 1), an apparently second-order phase transition is obtained by cooling in fields of $H < 3$ kG and corresponds to the a/f ordering discussed above. At low temperatures in a polydomain sample, as a magnetic field is applied the domain distribution is reduced from six to two at a field of $H \sim 2$ kG and the superlattice intensity begins to increase (Fig. 2). This corresponds to phase boundary II. When TmSe is cooled in a field of $H = 6$ kG only two domains are present and phase boundary II disappears. On reapplication of the field, the antiferromagnetic intensity decreases and the ferromagnetic intensity increases (Fig. 2). At a field of $H \sim 3$ kG the a/f intensity disappears and a metamagnetic transition occurs. From the magnetization measurements, this appears first order, but because of demagnetizing effects, the first-order nature may smeared out. The exact nature of all the transitions studied will require careful measurements on properly shaped samples with a homogeneous demagnetizing field. With this reservation, we arrive at the following picture of the phase diagram. Phase boundary III is a line of first-order metamagnetic transition separating the a/f and paraphases. Boundaries I and III meet at a multicritical point which is most likely a tricritical point. Line IV, which has been located by others, represents the points at which the bulk susceptibility is a maximum. This is not a true phase boundary, but, in our picture, represents an extension of the multicritical point into the paraphase.

Similar results to the above are obtained for applied fields in the (110) and (111) directions, in agreement with previous work.[5-8] As shown in Fig. 1, the metamagnetic transition fields are higher and indeed they scale approximately like the inverse cosine of the angle between a cube axis and the field direction.

The general behavior of the a/f and ferromagnetic moments at low fields may be readily understood using a classical spin Hamiltonian. For simplicity we consider a field-cooled sample with the field along (010), the tetragonal axis along (001) and, therefore, the spins along (100). Further we consider an effective spin Hamiltonian with a Zeeman term, a cubic anisotropy [only the nonvanishing terms are shown in Eq. (1)], and nearest-neighbor (nn) and next-nearest-neighbor

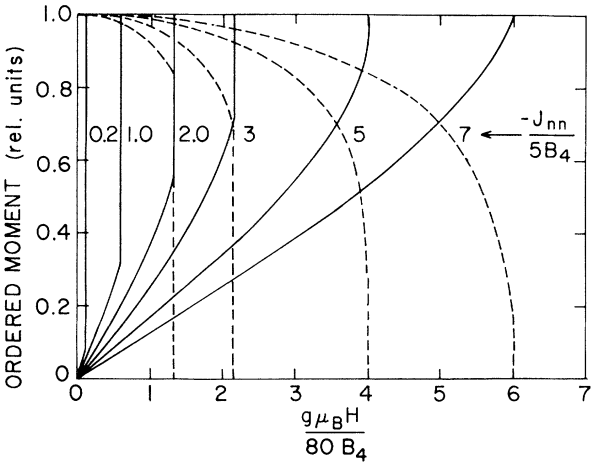

FIG. 3. Theoretical values for the ferromagnetic and antiferromagnetic (shown dashed) moment as a function of $g\mu_B H/80B_4$ for various values of the reduced exchange $-J_{nn}/5B_4$, calculated from Eqs. (2) and (3).

(nnn) isotropic exchange:

$$\mathcal{H} = \sum_i g\mu_B \vec{H}\cdot\vec{S}_i + \tfrac{5}{2}B_4 \sum_i (S_i^+)^4 + (S_i^-)^4 + \sum_{\langle nn\rangle} J_{nn}\vec{S}_i\cdot\vec{S}_m + \sum_{\langle nnn\rangle} J_{nnn}\vec{S}_i\cdot\vec{S}_m, \quad (1)$$

where the $\vec{S}_i$'s are unit classical vectors and $\vec{H}$ is the internal field. From the type-I structure, from T_N and the metamagnetic field one knows immediately that J_{nn} is weak and antiferromagnetic while J_{nnn} is much stronger and ferromagnetic. In a classical picture for the above configuration, as the field is increased the moments will rotate out of the (100) direction towards (010). If $90-\alpha$ is the angle between the magnetic moment and the field direction then, in the mean-field approximation for a type-I two-sublattice a/f, the angle-dependent energy per spin is

$$E = +4J_{nn}\cos 2\alpha - 5B_4\cos 4\alpha - g\mu_B H\sin\alpha. \quad (2)$$

The relationship between the rotation angle α and the field H at $T=0$ is then simply

$$\cos\alpha = 0 \quad (3a)$$

or

$$g\mu_B H = (-16J_{nn} + 80B_4\cos 2\alpha)\sin\alpha. \quad (3b)$$

We show in Fig. 3 the ferromagnetic and antiferromagnetic moments calculated from Eqs. (2) and (3) as a function of $g\mu_B H/80B_4$ for various values of $-J_{nn}/5B_4 \leq 5$. The condition for the transitions to be first order at $T=0$ is $-J_{nn}/5B_4 \leq 5$; for larger values one has a second-order transi-

tion.

We have not carried out the mean-field theory for finite temperatures. However, based on results for analogous metamagnetic models[10] it seems evident that, for $-J_{nn}/5B_4 \leq 5$, as the temperature in increased from $T=0$ the size of the first-order jump will decrease; the first-order line will ultimately terminate at a tricritical point T_t and for $T_t \leq T \leq T_N$ the transition will be second order.

It is clear that the above model and explicitly the curves in Fig. 3 reproduce qualitatively both our own experimental results as well as those of previous workers, most notably the pressure measurements by Guertin, Foner, and Missell.[5] In our sample we may estimate from our data and those of Walsh *et al.*[9] that at low temperatures H(first order) $\simeq$ 2.8 kG, and $\sin\alpha$(first order) $\simeq$ 0.4. Within the mean-field approximation one has $kT_N = -\frac{4}{3}J_{nn} + 2J_{nnn}$. From these three pieces of information we then deduce $B_4 \simeq 4\times10^{-4}$ meV, $J_{nn} \simeq -3\times10^{-3}$ meV, and $J_{nnn} \simeq 1.3\times10^{-1}$ meV. The values for B_4 and J_{nn} are markedly sample and pressure dependent while the dominant ferromagnetic exchange J_{nnn} seems to be somewhat less so.

The most surprising feature of the above results is that they are so simple. The mixed-valent effects play no obvious role in the magnetic phase diagram. Rather a simple symmetry-determined classical spin Hamiltonian accounts for all of the principal features of the magnetic data. A number of caveats are encountered, however, when one attempts to relate the classical spin picture to the real Hamiltonian. First, the ordered moment is extremely small and it increases very slowly as a function of field.[5,8] Previous workers[5-8] have suggested that the small moment originates in Tm^{3+} singlet–ground-state effects. However, based on experiments in analogous singlet–ground-state materials we would expect saturation of the moment at $(6-7)\mu_B$ for moderate fields. Instead the moment is only $\sim 4\mu_B$ at 150 kG.[8] Second, the crystal-field anisotropy is anomalously small and of opposite sign to that estimated on a point-charge basis and observed in related pnictide compounds. We should emphasize that no appreciable crystal-field splittings have been detected by any of specific-heat, elastic-constant,[7] or inelastic-neutron-scattering measurements. On the basis of the above facts, we believe that a singlet–ground-state explanation of the magnetism in TmSe is not tenable.

Our picture of TmSe in the mixed-valent (MV) state emerges as follows: At low temperatures, the effective moment is markedly reduced by the mixed-valent hybridization. Explicitly, but in greatly simplified terms, if we write $|MV\rangle = \alpha|3+\rangle + \beta|2+\rangle$ (in our sample $\alpha^2 = 0.8$ and $\beta^2 = 0.2$), then the cross term $2\alpha\beta\langle 3+|L_z+2S_z|2+\rangle$ must be of comparable magnitude but opposite in sign to the diagnonal component $\alpha^2\langle 3+|L_z+2S_z|3+\rangle + \beta^2\langle 2+|L_z+2S_z|2+\rangle$. Similarly, the crystal field, $\langle MV|\mathcal{H}_{CF}|\times MV\rangle$, is considerably reduced from $\langle 3+|\mathcal{H}_{CF}|\times 3+\rangle$ and indeed it is of opposite sign. We can estimate the magnitude of the hybridization energy as follows. Magnetic fields of 225 kG[2] are not sufficient to overcome the moment-reduction effect so that the mixed-valent spin fluctuation energy must exceed 10 meV. However, for temperatures >100 K the full moment seems to be obtained in the Curie-Weiss susceptibility; that is, the $|2+\rangle$ and $|3+\rangle$ states contribute incoherently. Both of these suggest a mixed-valent bandwidth of the order of 10 meV to within a factor of 2 or 3. This is consistent with estimates in other materials.[2]

We should like to thank K. Andres and W. M. Walsh for the loan of the TmSe sample. We should also like to acknowledge helpful discussions with the above as well as with J. Als-Nielson, E. Bucher, S. Foner, R. Guertin, H. A. Hook, and C. M. Varma.

This work was supported in part by the U. S. Energy Research and Development Administration under Contract No. EY-76-C-02-0016 and in part by the National Science Foundation.

---

[a]Permanent and present address: Risø National Laboratory, Roskilde, Denmark.

[1]For a review, see C. M. Varma, Rev. Mod. Phys. 48, 219 (1976).

[2]A comprehensive set of papers is given in *Valence Instabilities and Related Narrow-Band Phenomena*, edited by R. D. Parks (Plenum, New York, 1977).

[3]D. E. Cox, L. Passell, R. J. Birgeneau, and E. Bucher, unpublished. These results can now be understood by assuming a distribution of Tm valence states in their sample.

[4]E. Bucher, K. Andres, F. J. DiSalvo, J. P. Maita, A. C. Gossard, A. S. Cooper, and W. W. Hull, Jr., Phys. Rev. B 11, 500 (1975).

[5]R. P. Guertin, S. Foner, and F. P. Missell, Phys. Rev. Lett. 37, 529 (1976), and Ref. 2, p. 275.

[6]H. R. Ott, K. Andres, and E. Bucher, in *Magnetism and Magnetic Materials—1974*, AIP Conference Proceedings No. 24, edited by C. D. Graham, Jr., G. H. Lander, and J. J. Rhyne (American Institute of Physics, New York, 1975), p. 40.

[7]H. R. Ott, B. Luthi, and P. S. Wang, Ref. 2, p. 289.
[8]G. Chouteau, F. Holtzberg, J. M. Mignot, O. Pena, and R. Tournier, Ref. 2, p. 483.
[9]W. M. Walsh, Jr., K. Andres, L. W. Rupp, Jr., and L. D. Longinotti, Ref. 2, p. 499, and private communication.
[10]R. J. Birgeneau, G. Shirane, M. Blume, and W. C. Koehler, Phys. Rev. Lett. 33, 1098 (1974).

Boundary Conditions for Renormalization-Group Equations in One-Dimensional Fermi Gas

A. I. Larkin[a] and J. Sak[b]
Aspen Center for Physics, Aspen, Colorado 81611
(Received 7 September 1977)

The energy gap in one-dimensional Fermi systems with weak attractive interaction is expressed in terms of the parameters of the Hamiltonian and the electron density. The models of Hubbard and phonon-mediated interactions are studied in detail. The result for the Hubbard model is compared with numerical calculations.

As is well known, the energy spectrum of Fermi systems with attractive interaction has a gap. The purpose of this work is to derive an expression for the magnitude of the gap in a weakly interacting one-dimensional system. We obtain results for two systems: the Hubbard model and electron-phonon system.

The Hubbard Hamiltonian,

$$H=-T\sum_{i\sigma}(a_{i\sigma}^{\dagger}a_{i+1\sigma}+a_{i\sigma}^{\dagger}a_{i-1\sigma})+U\sum_{i}a_{i\uparrow}^{\dagger}a_{i\uparrow}a_{i\downarrow}^{\dagger}a_{i\downarrow}, \tag{1}$$

describes electrons on a lattice with nearest-neighbor hopping and interacting only when they are in one cell.

In the weak-coupling limit $|U/T|\ll 1$, $U/T<0$, our result for the energy gap is

$$\Delta=8(2/\pi)^{1/2}T\sin^2(\pi\rho/2)\sqrt{g}\,e^{-1/g}, \tag{2}$$

where ρ is the average number of electrons per cell, the dimensionless coupling constant g is defined as

$$g=U/v\pi,$$

and the Fermi velocity $v=2T\sin(\pi\rho/2)$.

The dependence of Δ on the coupling constant g can be obtained from the renormalization-group (RG) equations.[1-3] However, for the determination of the density-dependent factor in (2) it is necessary to know the boundary conditions for the integration of the RG equations.

In the RG method one integrates over those degrees of freedom which are characterized by wave vectors separated from the Fermi points by distances larger than some value k. The wave vector k is arbitrary but it is assumed that $k\ll k_F$, the Fermi momentum, so that the electronic spectrum is well approximated by a linear function of momentum. As a result one obtains an effective Hamiltonian which has the form

$$H_{\rm eff}=\sum_{|p|<k}vp(b_p^{\dagger}b_p-c_p^{\dagger}c_p)+\frac{\pi v}{L}\sum_{\substack{k_1k_2k_3k_4\\|k_i|<k}}\delta(k_1+k_2-k_3-k_4)[g_1b_{k_1\sigma}^{\dagger}c_{k_2\sigma'}^{\dagger}b_{k_3\sigma'}c_{k_4\sigma}+g_2b_{k_1\sigma}^{\dagger}c_{k_2\sigma'}^{\dagger}c_{k_3\sigma'}b_{k_4\sigma}$$
$$+g_3(b_{k_1\sigma}^{\dagger}b_{k_2\sigma'}^{\dagger}c_{k_3\sigma'}c_{k_4\sigma}+c_{k_1\sigma}^{\dagger}c_{k_2\sigma'}^{\dagger}b_{k_3\sigma'}b_{k_4\sigma})]. \tag{3}$$

The effective coupling constants depend on k and g_1 obeys the following RG equation

$$k\,dg_1/dk=g_1^2+\tfrac{1}{2}g_1^3+f(g_1), \tag{4}$$

where the first two terms were calculated by perturbation theory[3] and the function $f(g_1)$ is an unknown remainder about which we only need to know that for small g_1 it is of order (g_1).[4] We assume that the function f depends only on g_1 alone. This is consistent with the theories based on the bosonization of fermions[4] in which the Hamiltonian splits into two commuting parts, one of which contains only g_1. Equation (4) is valid when the