Observation of a hybridization energy gap in mixed-valent TmSe

S. M. Shapiro and B. H. Grier
Brookhaven National Laboratory, Upton, New York 11973
(Received 27 October 1981)

Inelastic neutron scattering studies have been performed on single crystals of TmSe. An excitation at $\hbar\omega \sim 10$ meV is observed whose momentum, temperature, and sample dependences provide evidence that this spectral features is due to an excitation across a hybridization gap in TmSe.

An important parameter in all discussions of the mixed valence problem is the quantity $\delta \equiv E_f - E_F$ which is the location of the $4f$ level relative to the Fermi level, E_F.[1] Many of the descriptions of the mixed valent state assume that δ is small or zero which implies that the f level is very close to or at the Fermi level.[2,3] If the symmetry is appropriate, there is an interaction between the localized f level and the bandlike conduction electrons and a hybridization gap develops in the electronic structure (see inset in Fig. 1). This was first proposed by Mott[4] in 1973 and expanded upon by Martin and Allen.[5] Its existence has been postulated to explain the increase in the low-temperature resistivities observed in SmB_6, SmX (X = S, Se, Te), and TmSe.[6] The effects of hybridization are manifested more clearly in these compounds since the only conduction electrons present are those originally from the $4f$ shell. Recent tunneling and infrared studies on SmB_6 indicate that a gap in the 5–8-meV range exists in SmB_6.[6]

In this Communication, we report the direct spectroscopic observation of a hybridization gap in a single crystal of TmSe by inelastic neutron scattering.[7] The gap is observed as a peak in the inelastic spectra at $\hbar\omega \approx 10$ meV.[8] The energy, temperature, and momentum dependences are all consistent with the recent calculations by Fedro and Sinha,[9] who predicted the neutron scattering cross section of such an excitation.

The experiments were performed on a single crystal of TmSe which was previously used to study the magnetic ordering in this compound.[10] The lattice parameter at room temperature is $a = 5.714$ Å and the material orders in a type-I antiferromagnetic structure at $T_N = 3.2$ K with a moment of $1.7\mu_B$. These properties indicate that we have a stoichiometric sample of TmSe. The inelastic neutron scattering measurements were performed on a three-axis spectrometer at the Brookhaven High Flux Beam Reactor. Because of the small sample size (~ 25 mm^3) relatively coarse resolution was used. We operated with a fixed final energy of 24.0 meV and a collimation of 40′ throughout the instrument. This gave an energy resolution of $\delta E = 2.0$ meV at zero energy transfer increasing to $\delta E = 2.7$ meV at 10-meV energy transfer.

The inelastic spectra of TmSe measured at $T = 4.6$ K for several q values along the $[q00]$ direction are shown in Fig. 1. The intensity is clearly a maximum at $\vec{Q} = (1,0,0)$, the zone boundary and decreases to about $\frac{1}{4}$ of its value at the zone center, $\vec{Q} = (2,0,0)$. The decrease due to form factor only accounts for 25% of the intensity change. There is about 2-meV dispersion of the frequency throughout the Brillouin zone. A similar behavior was observed along other symmetry directions.

The temperature dependence of this excitation is

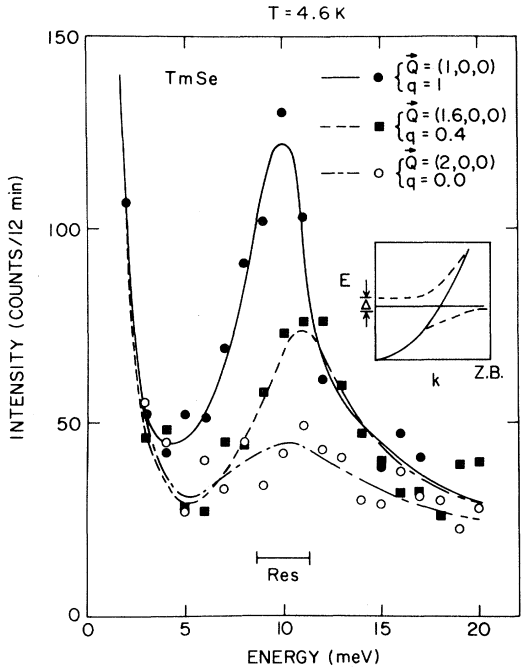

FIG. 1. Spectra of TmSe measured at $T = 4.6$ K for different values of q along the $[q00]$ direction. The inset is a schematic form of uncoupled f and d bands (solid lines) and the result when they are coupled giving rise to a hybridization gap Δ.

shown in Fig. 2 measured at $\vec{Q}=(1.25,0,0)$ which is $\frac{3}{4}$ of the way to the zone boundary. An attempt has been made to subtract the elastic background by taking the intense resolution limited signal at $\hbar\omega=0$ measured at $T=50$ K as the nonmagnetic background. The temperature dependence is very similar to that measured on a polycrystalline sample by Loewenhaupt and Holland-Moritz.[8] A sharp inelastic peak is observed at lower temperatures which broadens on heating and for $T>50$ K is indistinguishable from a quasielastic peak centered at $\hbar\omega=0$. In Ref. 8, a finite linewidth was reported at low temperatures but our observations on the single crystal show that the peak is resolution limited and any intrinsic broadening is estimated at less than 0.5 meV (half width at half maximum—HWHM). The 2-meV HWHM observed on the polycrystalline sample arises from the dispersive nature of the excitation.

Cooling the sample below $T_N=3.2$ K has no measurable effect on the inelastic peak at 10 meV. Another mode appears[8,11] at lower energies. This mode is most likely the antiferromagnetic magnon since its frequency tends toward zero as we approach the magnetic zone center. Unfortunately, the signal was too weak to probe this excitation in detail. A larger crystal is needed.

An additional experimental characteristic is the dependence of the 10-meV excitation on sample stoichiometry. Many of the properties of TmSe, including the valence, are strongly dependent upon the stoichiometry of Tm_xSe.[12,13] For $x<1$, the Tm valence increases toward 3+. Figure 3 shows the spectra of Tm_xSe measured at the zone boundary for two different values of x. The top portion is measured for $x=1.0$ and discussed above. The room-temperature lattice parameter is $a=5.714$ Å. The lower portion was obtained for a larger crystal with $a=5.690$ Å. This converts to $x=0.99$ using the results of Ref. 12. It is clearly seen that the peak is much broader in the sample that is Tm deficient than the stoichiometric sample. Inelastic studies already published[14] on a sample with $a=5.645$ Å ($x\simeq 0.90$) show no evidence of any well-defined excitation but only a broad peak centered around $\hbar\omega=0$.

An interpretation of this excitation as a crystalline electric field excitation does not seem appropriate. First, the energy is much too large to be due to crystal-field splitting of the ground state of the Tm ion. It is almost four times the Γ_1-Γ_4 splitting observed in TmAs, a compound with the same structure and almost identical lattice parameter.[15] It is about 10 times larger than the value estimated from the magnetic field dependence of the ordering at low temperatures.[10] Secondly, the large variation of in-

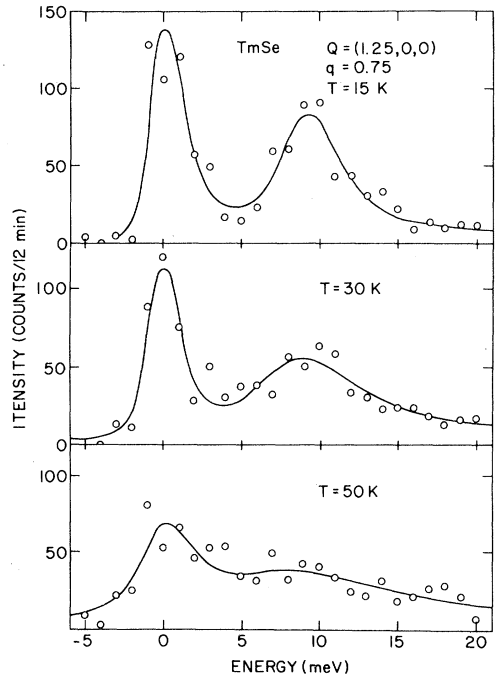

FIG. 2. Temperature dependence of the inelastic spectra of TmSe measured at several temperatures. A constant energy-independent background has been subtracted plus a resolution-limited elastic part measured at $T=50$ K.

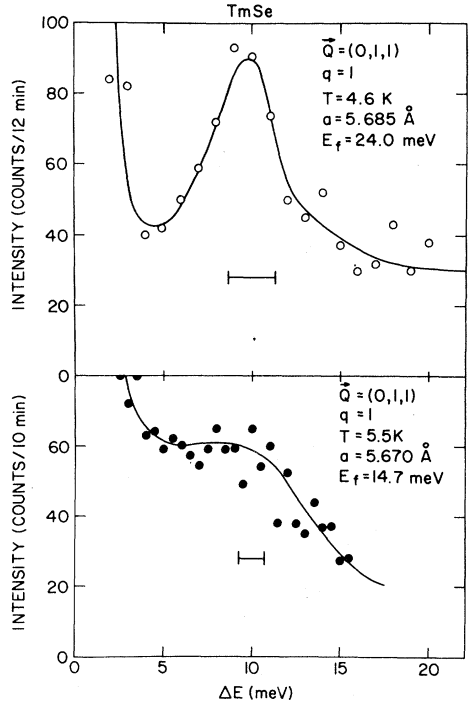

FIG. 3. Inelastic spectra measured for two samples of TmSe at low temperature. The top portion is for $Tm_{1.0}Se$ and the lower is for $Tm_{0.99}Se$. The concentrations were determined by the room-temperature lattice constant.

tensity within a given Brillouin zone is inconsistent with the expected behavior of a crystal-field excitation in rare-earth based systems. Thirdly, other excitations should be present due to the splitting of the orbital degeneracy and none has been observed.[8] Finally, one would not expect a 1% change in stoichiometry to drastically change the crystalline electric field parameters.

We interpret the excitation at $\hbar\omega = 10$ meV as arising from the excitation across the hybridization gap originating from the coupling between the localized f electron and bandlike d electron as shown schematically in the inset in Fig. 1. The telltale feature of our results which strongly suggests this origin is the strong momentum dependence of the intensity: being strongest at the zone boundary and weakest at the zone center. This occurs because the electron density of states is large near the zone boundary and the zone center. Thus one obtains the maximum intensity at wave vectors which span the Brillouin zone (see inset in Fig. 1). For $\vec{q} = 0$ transitions, i.e., vertical transitions, one does not find simultaneously a large density of states for the initial and the final states. The temperature dependence is also consistent with this interpretation in that broadening as T increases is due to the smearing of the Fermi function as T increases.

The sensitivity of this excitation to the stoichiometry also suggests that the 10-meV excitation is related to an excitation across a hybridization gap. By changing the stoichiometry we are most likely changing the position of the f level relative to the Fermi level. This changes dramatically the mixed-valent properties and, as we have seen above, the nature of the observed excitation. These results are also supported by the fact that the resistivity of Tm_xSe is strongly dependent on x and decreases as x decreases implying a change in the nature of the f-d hybridization,[12] and a reduction of the gap.

These features were independently predicted by Fedro and Sinha, who calculate the neutron scattering cross section for a mixed valent system.[9] They find a peak in the spectra near Δ, where Δ is the hybridization gap. The position of the peak shows little $\vec{q}$ dependence and the intensity is a maximum at the zone boundary and decreases as $\vec{q} \to 0$. Also the linewidth increases as T increases. They also find a quasielastic peak which increases as the temperature is lowered. All these features are found in our experimental study of TmSe.

In conclusion, we have presented evidence which strongly supports the existence of a hybridization gap in TmSe. It manifests itself in a sharp peak at $\hbar\omega = 10$ meV whose intensity is strongly dependent on momentum, temperature, and sample quality and follows the predictions of recent calculations.[9] The existence of a gap contrasts with theoretical studies which predict that there should be no hybridization gap in paramagnetic TmSe, but there may be one in antiferromagnetic TmSe.[5] It will be of interest to study the behavior of the excitation with higher resolution to see if there is an effect when TmSe orders antiferromagnetically.

The authors are indebted to A. J. Fedro and S. K. Sinha for communicating their theoretical predictions prior to publication and for letting us use their model. We also thank P. Bak, B. Batlogg, H. R. Ott, R. D. Parks, and C. M. Varma for useful discussions. Work was supported by the Division of Basic Energy Sciences, U. S. Department of Energy, under Contract No. DE-AC02-76CH00016.

[1]C. M. Varma, Rev. Mod. Phys. 48, 219 (1976).
[2]See papers, in *Valence Instabilities and Related Narrow Band Phenomena,* edited by R. D. Parks (Plenum, New York, 1977).
[3]*Valence Fluctuations in Solids,* edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, New York, 1981).
[4]N. F. Mott, Philos. Mag. 30, 403 (1973).
[5]R. M. Martin and J. W. Allen, J. Appl. Phys. 50, 7561 (1979).
[6]B. Batlogg, P. H. Schmidt, and J. M. Rowell, Ref. 3, p. 267.
[7]A preliminary account was given by B. H. Grier and S. M. Shapiro, Ref. 3, p. 325.
[8]This excitation was originally observed in a polycrystalline sample by M. Loewenhaupt and E. Holland-Moritz [J. Appl. Phys. 50, 7456 (1979)] but its origin was unclear.
[9]A. J. Fedro and S. K. Sinha, Ref. 3, p. 329.
[10]H. Bjerrum-Møller, S. M. Shapiro, and R. J. Birgeneau, Phys. Rev. Lett. 39, 1021 (1977).
[11]M. Loewenhaupt and H. Bjerrum-Møller, in Proceedings of the Conference on Low Temperature Physics, LT-16 (in press).
[12]B. Batlogg, H. R. Ott, W. Thone, and P. Wachter, Phys. Rev. B 19, 247 (1979).
[13]P. Haen, F. Lapiene, J. M. Mignot, R. Tournier, and F. Holtzberg, Phys. Rev. Lett. 43, 304 (1979).
[14]S. M. Shapiro, H. B. Møller, J. D. Axe, R. J. Birgeneau, and E. Bucher, J. Appl. Phys. 49, 2101 (1978).
[15]H. L. Davis and H. A. Mook, in *Magnetism and Magnetic Materials—1973 (Boston),* edited by C. D. Graham and J. J. Rhyne, AIP Conf. Proc. No. 18 (AIP, New York, 1974), p. 1068.