PHYSICAL REVIEW B VOLUME 32, NUMBER 3 1 AUGUST 1985

Large ternary-metal contributions to the wave functions at the Fermi level in $TlMo_6Se_8$

R. F. Bell, F. J. DiSalvo, and R. G. Dunn
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

J. M. Tarascon
Bell Communications Research Inc., Murray Hill, New Jersey 07974

(Received 22 February 1985)

Previous crystallographic studies of Chevrel phases containing the ternary metals thallium or indium suggested that these metals were of "mixed valence." Here, we conclusively show that the Tl *s* band lies at the Fermi level, since large Knight shifts (~2.4%) of the ^{205}Tl NMR spectra in $TlMo_6Se_8$ are observed. This observation may help explain the high superconducting critical temperature of $TlMo_6Se_8$ (12.2 K) and the unique rhombohedral-to-rhombohedral structural phase transitions observed in $InMo_6S_{8-x}Se_x$ compounds.

The physical properties of the ternary molybdenum chalcogenides, commonly known as Chevrel phases, have been intensively investigated because of their unusual superconducting behavior.[1] In particular, some of these compounds have the highest critical magnetic fields of any known superconductor and still others exhibit reentrant superconductivity or the coexistence of antiferromagnetism and superconductivity.[2,3] Self-consistent band-structure calculations have been carried out for the cases where the ternary element is a rare-earth element or tin.[4] In those cases the wave functions at the Fermi level have very little ternary-element character. This observation explains why the magnetic moment of the rare-earth atoms has such a weak effect on the superconductivity. However, these results have led to the generalization of this observation; namely, that the ternary elements can be considered ions that donated their valence electrons to the Mo *d* band and that the wave functions at the Fermi level have no ternary-metal character for any possible ternary metal.[1,2] In this sense, the ternary element would be "electronically inert."

In a previous paper,[5] we suggested from crystallographic data that when the ternary metal is thallium or indium the Fermi level must cut through the ternary metal *s*-band. That is, the wave functions at the Fermi level must have considerable ternary-metal character. In this paper, we demonstrate by NMR measurements that this is correct. The existence of this ternary-metal band at the Fermi level may be responsible for the new behavior observed in these particular compounds. For example, $TlMo_6Se_8$ has the highest superconducting T_c of any selenide Chevrel phase (12.2 K) and the $InMo_6S_{8-x}Se_x$ series exhibits unique rhombohedral-to-rhombohedral structural phase transitions as a function of temperature or composition.[5,6]

The samples were prepared as previously described.[5,6] NMR measurements were performed on powder samples using a pulsed spectrometer with signal averaging. The persistent magnetic field produced by a superconducting magnetic and the sweep field were calibrated by using the resonance of deuterium in D_2O. We calculated the shift (K_n) of any spectral feature in the following way:

$$K_n = 100\left[\frac{\nu}{\gamma H} - 1\right],$$

where ν represents the frequency of the rf pulses, γ represents the gyromagnetic ratio (2457.0 Hz/G for ^{205}Tl), and H represents the magnetic field at which a given feature in the spectrum occurs.

In a typical run the magnetic field was approximately 25.8 kG and the resonance frequency near 65 MHz. The shifts calculated by this method agree with those reported using 1.0 molar thallium acetate solutions as a standard within 0.01%.[7]

At low temperatures the spectrum consists of an asymmetric line typical of the powder pattern produced by a nucleus in a unique axially symmetric site.[8] The observed spectrum is considerably broadened from the ideal powder pattern. The broadening is approximately characterized by a Gaussian of full width at half maximum of about 25 G at 10 K. The peaks or shoulders of the asymmetric line determine the principal values of the shift tensor, and these are plotted in Fig. 1 versus temperature. (Under the above conditions the separation of the two characteristic features is about 120 G.) The shifts obtained from this pattern (Fig. 1) are larger than any values previously reported for thallium or its compounds. Such shifts are largest in metals, where the partially filled *s* states produce a large Knight shift. For example, thallium metal has a hexagonal structure and thus has two principal Knight shifts, 1.56% and 0.166%,[9] while the isotropic shift seen in TlV_5S_8 is about 0.5%.[10] In contrast, the shifts seen in typical monovalent or trivalent salts where there are no partially filled *s* states are from 0.0 to 0.3%.[7] We also measured the shift in the closely related phase $TlMo_6Se_6$.[11] From the measured Tl-Se bond lengths, Tl is expected to be monovalent in $TlMo_6Se_6$. Indeed, the measured Knight shift is $-0.005\pm0.01\%$, confirming that

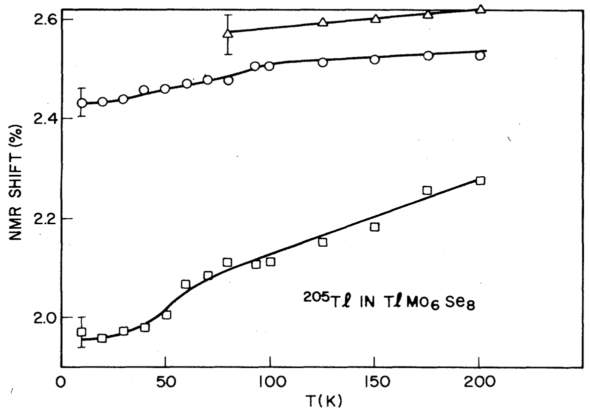

FIG. 1. Three components of the ^{205}Tl Knight shift in $TlMo_6Se_8$ are shown vs temperature.

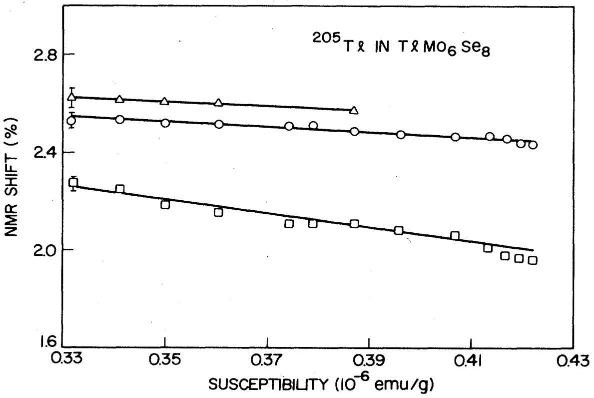

FIG. 2. The Knight shift plotted vs static magnetic susceptibility with the temperature as an implicit parameter.

the s states are full or equivalently that the Tl is monovalent.

The shifts are temperature dependent as expected, since the susceptibility is also temperature dependent.[6] However, the temperature dependences have the opposite sense, the susceptibility increases with decreasing temperature while the shifts decrease. This observation is unusual for situations where the s contribution dominates the Knight shift, and implies either significant p or, less likely, d character at the Tl site[12] or possibly a reduction in the local Tl susceptibility even while the total susceptibility increases. The more rapid change in the shift near 80 K is also seen in the susceptibility, so that the usual susceptibility shift plot (Fig. 2) produces straight lines. Similar shifts are observed for the sulfide analog $TlMo_6S_8$; however, the spectra are much broader and we do not discuss them here.

As the temperature is increased from 10 K, the broadening decreases and a third feature becomes apparent in the spectrum. It is not clear whether this third feature exists at low temperatures, and is masked by the broadening, or, if this feature develops upon increasing the temperature. This third feature, which is readily apparent above 100 K is entirely unexpected, since large atoms, such as, thallium, are thought to occupy sites on the $\bar{3}$ axis of the unit cell.[1] This site is axially symmetric and thus would allow only two components to the Knight shift as seen at low temperature. This means that at temperatures above approximately 80 K, some of the thallium atoms must move off the $\bar{3}$ axis. This movement could be static or dynamic, although in the latter case the motion would have to rather slow (on the order of the reciprocal linewidth). Such a movement off the $\bar{3}$ axis could also be expected to cause the unit cell to distort to a structure with a low symmetry, such as, monoclinic or triclinic. Such structural distortions are common in Chevrel phases,[1,2] although the driving force for such phase transitions may also involve the splitting of electronic degeneracies in the Mo-based d band. However, in all these other cases the high-symmetry structure transforms to the low-symmetry structure on decreasing the temperature. Powder x-ray-diffraction patterns taken using a rotating anode source showed that the sample had the expected rhombohedral structure at both room temperature and 12 K. The high intensity of the source gave a signal to noise of about 10^4 for the most intense peaks. At this level no new peaks or indications of line splittings were observed at room temperature or at 12 K that would indicate any distortion from the rhombohedral structure. The small changes in lattice parameters on warming from 12 K are consistent with the expected thermal expansion. These factors lead us to suggest that the development of the third component in the Knight shift is due to a thermally activated population of sites off the $\bar{3}$ axis, but in some uncorrelated fashion so that expected distortions from hexagonal symmetry are only short range. Such a displacement from the $\bar{3}$ axis is common for small ternary ions,[1] but not for large ions such as Tl (and Tl is the *largest* ternary ion that has been incorporated in the Chevrel phases).[5]

In summary, NMR measurements confirm the prediction from crystallographic data that the Fermi level must lie in the thallium s band, since a large Knight shift of the Tl in $TlMo_6Se_8$ is observed. This is the first Chevrel compound in which it has been shown that the ternary-metal wave functions make important contributions to the states at the Fermi level. We also found that the spectrum has three features at temperatures above about 100 K, suggesting that all of the thallium atoms are not centered on the crystallographic $\bar{3}$ axis, except, perhaps, at low temperatures.

We would like to thank R. E. Walstedt and W. W. Warren, Jr., for encouragement and discussions concerning the NMR measurements and R. M. Fleming for advice concerning the x-ray-diffraction measurements.

[1] K. Yvon, Curr. Top. Mater. Sci. **3**, 53 (1979).

[2] Ø. Fischer, Appl. Phys. **16**, 1 (1978).

[3] M. Ishikawa and Ø. Fischer, Solid State Commun. **24**, 501 (1977).

[4] T. Jarlborg and R. J. Freeman, Phys. Rev. Lett. **44**, 178 (1980).

[5] J. M. Tarascon, F. J. Di Salvo, J. V. Waszczak, and G. W. Hull, Jr., Phys. Rev. B **31**, 1012 (1985).

[6] J. M. Tarascon, F. J. Di Salvo, D. W. Murphy, G. W. Hull, Jr., and J. V. Waszczak, Phy. Rev. B **29**, 172 (1984).

[7] S. Hafner and N. H. Nachtrieb, J. Chem. Phys. **40**, 2891 (1964).

[8] N. Bloembergen and T. J. Rowland, Acta Metall. **1**, 731 (1953).

[9] N. Bloembergen and T. J. Rowland, Phys. Rev. **97**, 1679 (1955).

[10] W. Schramm, R. Schollhorn, H. Eckert, and W. Muller-Warmuth, Mater. Res. Bull. **18**, 1283 (1983).

[11] M. Potel, R. Chevrel, and M. Sergent, Acta Crystallogr., Sect. B **36**, 1545 (1980).

[12] J. Winter, *Magnetic Resonance in Metals* (Oxford University Press, New York, 1971), p. 114.