JOURNAL OF SOLID STATE CHEMISTRY 16, 197–200 (1976)

Magnetic Susceptibility and Nuclear Resonance Studies of $Tb_xY_{1-x}P$*

ROD K. QUINN AND H. T. WEAVER

Sandia Laboratories, Albuquerque, New Mexico 87115

Received June 20, 1975; in revised form July 23, 1975

Magnetic susceptibility and nuclear resonance of ^{31}P studies have been made for $Tb_xY_{1-x}P$ ($x = 0.005$, 0.05, 0.10, and 0.30) in the temperature range from 4 to 300°K. In this concentration range cooperative magnetic effects are small and the susceptibility is essentially determined by free Tb spins. However, the resonance lines are very broad and the uniform spin polarization model is found inapplicable.

I. Introduction

Transitions from Van Vleck paramagnetism to antiferromagnetism (*1*) in rare earth (*RE*) intermetallic compounds are driven by *RE–RE* exchange. The strength of this interaction depends on the density of *RE* spins and, consequently, is very sensitive to the *RE* concentration in the compound. A convenient method for investigating such a transition is to dilute the *RE* concentration by substituting either La or Y, which are chemically very similar to the *RE* elements but have no *f*-electrons. Magnetization studies of the resulting compounds clearly exhibit the transition.

A possible alternative method for studying these systems is to measure the Knight shift (K) of some convenient nucleus in the compound. Knight shift measurements for the nonmagnetic constituent of *RE* pnictides (*2*) showed that K is proportional to the susceptibility. Thus, the crystal field splitting and Curie–Weiss temperature can be determined from NMR and the effects of magnetic impurities on bulk measurements is overcome. In addition, for systems in which the *RE* exhibits a ground state singlet, the *RE* resonance, as well as that for the nonmagnetic nuclei, often can be detected (*3*). Thus, in principle, the local magnetization can be studied at two different atomic sites.

Further motivation for studying Van Vleck paramagnetism has recently been provided by NMR (*4*) and susceptibility (*5*) pressure experiments on Pr and Tm compounds. For some of these materials the volume dependence of the crystal field splitting is anomalous. Additional work on the related systems TbP and/or HoP is immediately suggested, except that these compounds order magnetically at temperatures such that crystal field effects are insignificant. Diluting these compounds with Y or La may allow low temperature studies of the Tb and Ho crystal field.

The problem with using NMR on random alloys is that the inherent sample inhomogeneity leads to line broadening (*6*, *7*), which affects the determination of K. However, it has been shown (*6*) that K often tracks χ even though the linewidth becomes large. Whether or not this broadening prohibits use of the resonance method in alloy intermetallics such as these has not been established. To investigate this situation we carried out susceptibility and Knight shift measurements on the series of compounds $Tb_xY_{1-x}P$ with $x = 0.005$, 0.05, 0.10, and 0.30. The compounds are cubic and Tb^{3+} exhibits a singlet ground state. Further-

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* This work supported by the U.S. Energy Research and Development Administration, ERDA.

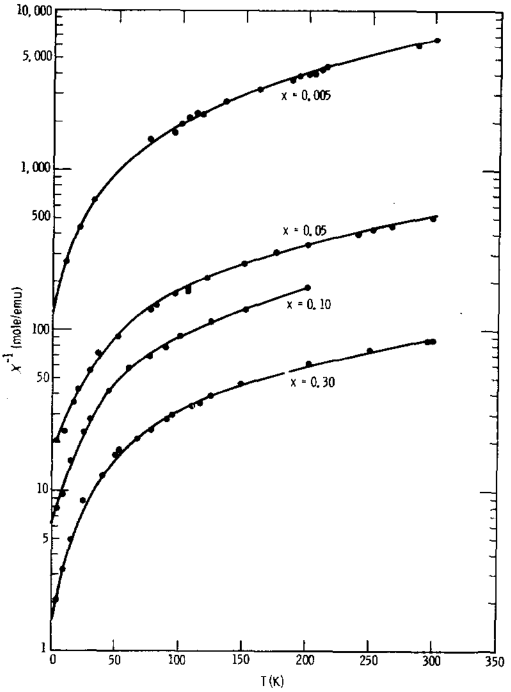

FIG. 1. Temperature dependence of the inverse sus-susceptibility for four samples of $Tb_xY_{1-x}P$. The data are plotted on semilog plot for display purposes.

more, for $x = 1$ the system orders antiferromagnetically at about 15°K so that the transition temperature can be affected by varying x.

TABLE I

SUMMARY OF CURIE–WEISS TEMPERATURES (θ) AND EFFECTIVE MOMENTS (p) FOR A SERIES OF $Tb_xY_{1-x}P^a$

x	θ (°K)	p (μ_B)
0.005	−5(2)	9.8(5)
0.05	−6(2)	9.5(2)
0.10	−6(2)	9.6(2)
0.30	−12(2)	9.4(2)

[a] The numbers in parentheses represent the error in the last quoted digit.

II. Experimental Method and Results

Samples were prepared by first arc melting the proper alloy ratio of Tb and Y. The resulting alloy was ground into a powder, mixed with P, sealed in a quartz pressure vessel, and heated for several days. The resulting compounds were ground into powder and annealed. X-ray powder diffraction patterns confirmed the existence of a single cubic phase.

Susceptibility measurements were carried out using the Faraday technique (8). The samples were coated with high purity, low vapor pressure oil to prevent reaction with air

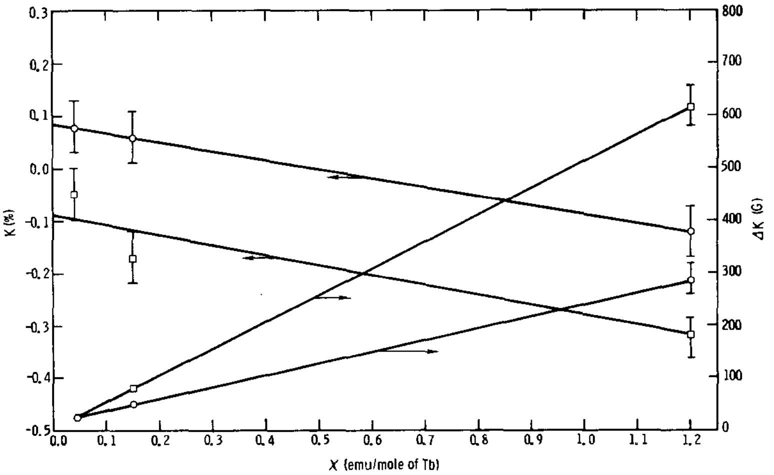

FIG. 2. Knight shift and linewidth for ^{31}P in two samples [(○) $x = 0.05$ and (□) $x = 0.10$] of $Tb_xY_{1-x}P$ as a function of susceptibility. The susceptibility is normalized to the number of Tb spins.

TABLE II

SUMMARY OF KNIGHT SHIFT (K) AND LINEWIDTH (ΔK) DATA FOR ^{31}P CONTAINED IN $Tb_xY_{1-x}P$.[a]

	$x = 0.005$		$x = 0.05$		$x = 0.10$	
T (°K)	K (%)	ΔK (G)	K (%)	ΔK (G)	K (%)	ΔK (G)
4	0.10(3)	35(5)	0.08(4)	27(5)	−0.05(4)	30(5)
77	0.10(3)	27(5)	0.04(4)	50(5)	−0.17(4)	80(8)
300	0.10(3)	35(5)	−0.12(4)	291(9)	−0.32(4)	620(10)

[a] The number in parentheses represents the error in the last quoted digit.

during the course of the experiment. The experimental susceptibility was then corrected for measured gram susceptibility of the oil, the diamagnetic behavior of which was verified to 4°K. Nuclear resonance was detected using both cw and pulse methods. Most of the data were taken at 20 MHz using pulse techniques.

Figure 1 shows the inverse molar susceptibility for the four samples. The effective moments and Curie–Weiss temperatures are given (*9*) in Table I. For $x = 0.005$, the diamagnetic susceptibility of YP made a significant contribution and to obtain a linear Curie–Weiss plot the value $\chi_{\text{dia}}(\text{YP}) = -0.55 \times 10^{-4}$ emu/mole was required. The quantities listed in Table I are found by appropriately correcting for χ_{dia} of YP.

Nuclear resonance could only be detected for ^{31}P and $x < 0.30$ due to severe line broadening, which is found to increase more rapidly than χ (see Fig. 2 and Table II) as $T \to 0$. Undoubtedly similar broadening, together with possible fast relaxation rates, prevented the observation of the Tb resonance in all samples.

III. Discussion

Within the molecular field approximation, cooperative magnetic effects are evidenced in the susceptibility by the shift in χ^{-1} by a fixed amount (*1*) as

$$\chi^{-1} = \chi_{CF}^{-1} - \lambda, \tag{1}$$

where χ_{CF} is the crystal field susceptibility and λ is the molecular field constant. The Curie–Weiss temperature is proportional to λ, which is assumed to scale linearly with x. However, only for $x = 0.3$ does the shift in χ (normalized to the number of Tb atoms) become detectable (see θ in Table I). On the other hand, the NMR already shows extreme broadening.

In Fig. 2 we plot the ^{31}P Knight shift (K) and the linewidth versus the susceptibility. Even in these low concentration samples, the linewidth has become large compared to K, which makes shift determinations inaccurate. Furthermore, the observation that K is different for a given susceptibility directly violates the uniform spin polarization model (*10*), which is often used to analyze *RE*-pnictide data. We now examine this point in more detail.

Conduction electron spin polarization arises from interactions of the conduction electrons with the f-electron spin, $\langle S \rangle$. In the uniform polarization model the field at each nuclear site is proportional to $\langle S \rangle$ and is independent of the number of *RE* ions. Specifically, we can write (*10*)

$$K = K_0\,[1 + \Gamma(g_J - 1)\chi/2N_f g_J \mu_B^2], \tag{2}$$

where Γ is the interaction strength, χ is the system susceptibility (mainly due to f-electrons), and N_f is the number of *RE* ions. Since χ is proportional to N_f, Eq. (2) predicts that the Knight shift is concentration (x) independent. In Fig. 2, we have essentially plotted K versus χ/N_f. Obviously, the model does not hold since K is different for two samples at a given χ/N_f. In contrast, the susceptibility scales nicely in that χ/N_f is the same for all samples, i.e., the effective moment (p) is constant; see Table I.

In addition to the failure of K to scale as χ/N_f we note that the hyperfine field, defined as $\Gamma K_0/2\mu_B$ and found from $dK/d\chi$, is three orders of magnitude less than that in TbP. This suggests that a large part of the magnetization is produced by appreciable spin densities near the Tb nuclei and the nearby P spins are "wiped out," i.e., shifted by large amounts. Again, uniform polarization is a poor approximation to such a situation.

In conclusion, we find that severe inhomogeneous broadening, due to the random distribution of Tb spins, limits the usefulness of NMR when applied to mixed intermetallic compounds. The bulk susceptibility is accurately described by a collection of free Tb spins, but the resulting conduction electron polarization is not even approximately uniform.

Acknowledgments

The authors are grateful to P. G. Neiswander and B. R. Hansen for valuable technical assistance.

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