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NEUTRON MEASUREMENT OF CRYSTAL FIELD SPLITTINGS IN TmAs AND TmBi*

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ABSTRACT

Analyses of inelastic neutron data collected for TmAs (TmBi) have determined the Lea-Leask-Wolf parameters to be $x = -0.79$ (-0.81) and $W = -0.106$ (-0.0736) meV. These results are discussed relative to a nearest-neighbor point-charge model, and to their usefulness in establishing a correlation between crystal-field quantities and ligand electronegativity.

INTRODUCTION

Neutron scattering has been, and is continuing to be, applied to obtain crystal-field information for a variety of rare-earth based solids. Of particular interest for this work are investigations[1-5] on some compounds in the RX class, defined to contain all the NaCl-structured rare-earth monopnictides (N, P, As, Sb, Bi) and monochalcogenides (S, Se, Te). One value of the resulting data has been its reduction to obtain parameters specifying the crystal-field splitting of the ground J-multiplet of the respective $4f^n$ configurations. Such parameters have their basis in the Hamiltonian[6]

$$H = W\{[x/F(4)]\ O_4 + [(1-|x|)/F(6)]\ O_6\} . \qquad (1)$$

The operator equivalences $O_4/F(4)$ and $O_6/F(6)$ have forms dictated only by the cubic symmetry and the considered J value. W is related to the overall crystal-field splitting of the multiplet and x $(-1 \leq x \leq 1)$ to the ratio of the fourth to sixth-order terms. Thus, W and x are parameters which completely specify the crystal-field.

Having available empirically extracted crystal-field parameters opens the possibility of their being useful in providing both direct and indirect explanations for the RX compounds' various properties. Besides being of value in providing consistent "explanations" for some of the compounds' physical properties (e.g., magnetic susceptibilities and specific heats), knowledge of these parameters may also prove to be useful in discovering which fundamental processes are dominant in the formation of the compounds' electronic structure. In fact, when studies have been made of trends in the parameters over a series of compounds, some interesting observations have emerged. Among these are the close quantitative relationships found between empirical parameters and values predicted by simple point-charge models,[2-5] and correlations observed between the parameters and

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electronegativity of the ligands.[7,8] Obtaining crystal-field parameters for more RX compounds may enable these observations to be expanded to include the new results, or the new results may show that an observation has only a limited application. In this spirit we decided to investigate TmAs and TmBi, and our neutron results and their analyses are reported here.

For small momentum transfers the cross-section for neutrons scattering from an isolated J-multiplet follows the proportionality[9]

$$\partial^2\sigma/\partial\Omega\partial\omega \sim (k_f/k_i)\, F^2(\vec{Q}) \sum_{n,m} \rho_n \left|\langle n|\vec{J}_\perp|m\rangle\right|^2 \delta(\varepsilon_{nm} - \hbar\omega) \quad . \qquad (2)$$

The crystal-field levels $|n\rangle$ and $|m\rangle$ have an energy difference ε_{nm}, with the δ-function indicating that the neutron suffers a gain or loss, $\hbar\omega$, in its kinetic energy according to the sign of ε_{nm}. The component of $\vec{J}$ perpendicular to the scattering vector $\vec{Q}$ is $\vec{J}_\perp$, while $F(\vec{Q})$ is the magnetic form factor. The momenta of the incident and scattered neutrons are k_i and k_f, while ρ_n is a Boltzmann factor.

The ground multiplet of the $4f^{12}$ configuration for Tm^{3+} is $^3H_6$, and the Hamiltonian (1) will split its 13-fold degeneracy into 3 triplets Γ_4, $\Gamma_5^{(1)}$, $\Gamma_5^{(2)}$, a doublet Γ_3, and two singlets Γ_1 and Γ_2. The relative energetic ordering of these Γ_i will depend upon the value of x and the sign of W. Although no fundamental reasons existed as to what these parameters would be for TmAs and TmBi, previous specific heat and susceptibility measurements, point-charge model estimates, and neutron results on TmSb, all suggested that the ordering should be Γ_1, Γ_4, $\Gamma_5^{(2)}$, Γ_2, $\Gamma_5^{(1)}$, and Γ_3 in order of increasing energy. Indeed this is the order determined in the present work.

RESULTS AND DISCUSSION

Our experiments used the Oak Ridge magnetically-pulsed time-of-flight spectrometer.[10] After pulsing and monochromating, the beam is scattered by the sample and detected by high-pressure ^3He detectors.

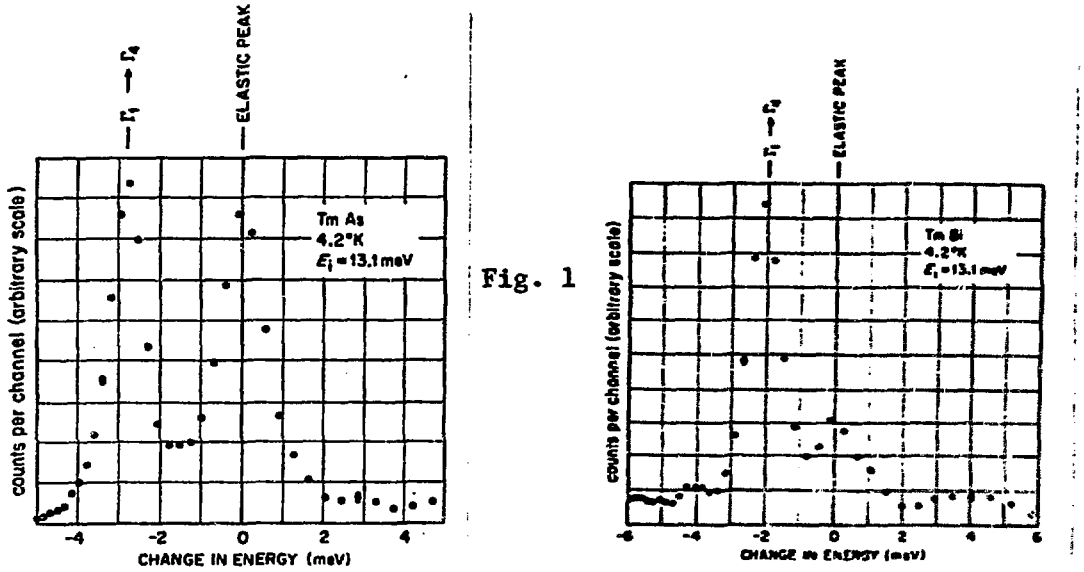

Fig. 1

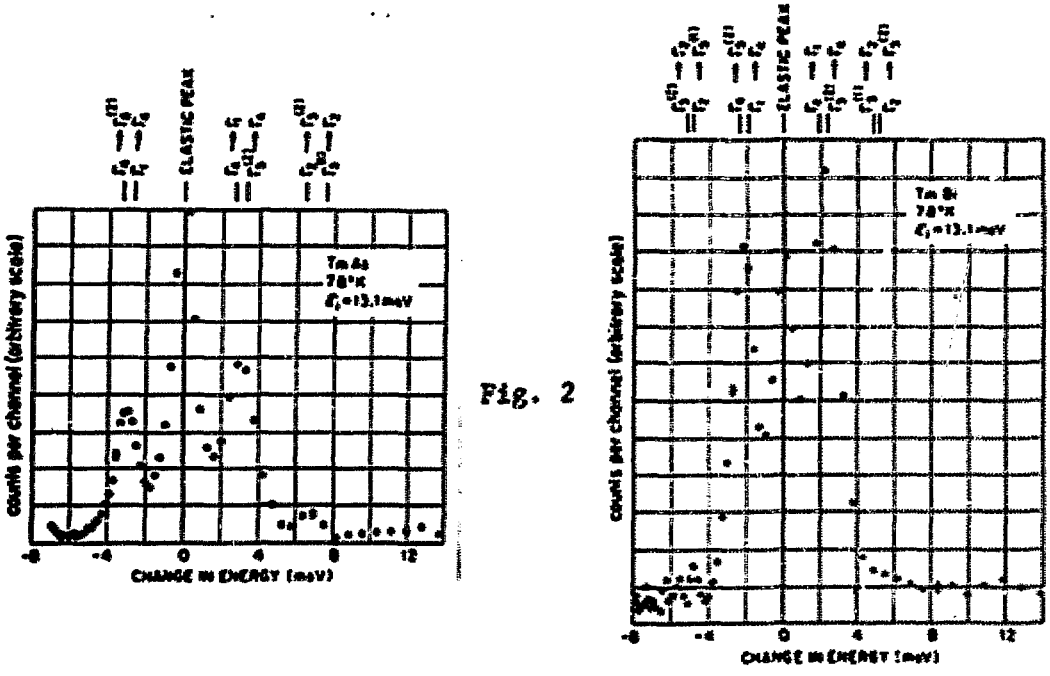

Fig. 2

The time distribution of neutrons arriving at a detector is recorded, and cross-correlation techniques applied between the pseudorandom pulsing signal and the time distribution enables data of counts vs. time-of-flight channel (or energy) to be obtained. The TmAs and TmBi samples each consisted of about 3 cc. of powder furnished by D. E. LaValle.[11] Data using an incident neutron energy, E_i, of 13.1 meV are in Figs. 1 thru 3. The energies of the data points correspond to the average times of the channels, with a positive (negative) energy representing neutrons gaining (losing) kinetic energy. The points are not evenly spaced in energy since the data channels were set to have constant-time widths rather than constant-energy widths. The zero energy peaks correspond to neutrons elastically scattered from the samples due to nuclear elastic scattering processes and to quasielastic crystal-field scattering.

At the top of each figure are indicated transitions obtained by fitting the data to a model based on Eqs. (1) and (2). The model contained the parameters W and x, and a level-width parameter which introduced an energy smearing of the Γ_i levels. For a given compound and temperature, the same amount of Gaussian smearing was applied to each Γ_i. A computer program calculates the eigenvalues and eigenfunctions of Eq. (1), and then the $\rho_n|\langle n|J_\perp|m\rangle|^2$ factors of Eq. (2). The Γ_i are then Gaussian smeared, and the cross-section of Eq. (2) calculated as a function of $\hbar\omega$. The cross-section is then convoluted with the measured instrumental resolution which varies with $\hbar\omega$. To obtain relative values of theoretical counts per channel, the convolution results are integrated over each channel's energy-width. After subtracting a flat parametric background from the experimental values, theoretical counts are compared with experimental counts. The above calculational process does not include any contribution from nuclear elastic scattering processes, so those channels which lie in the vicinity

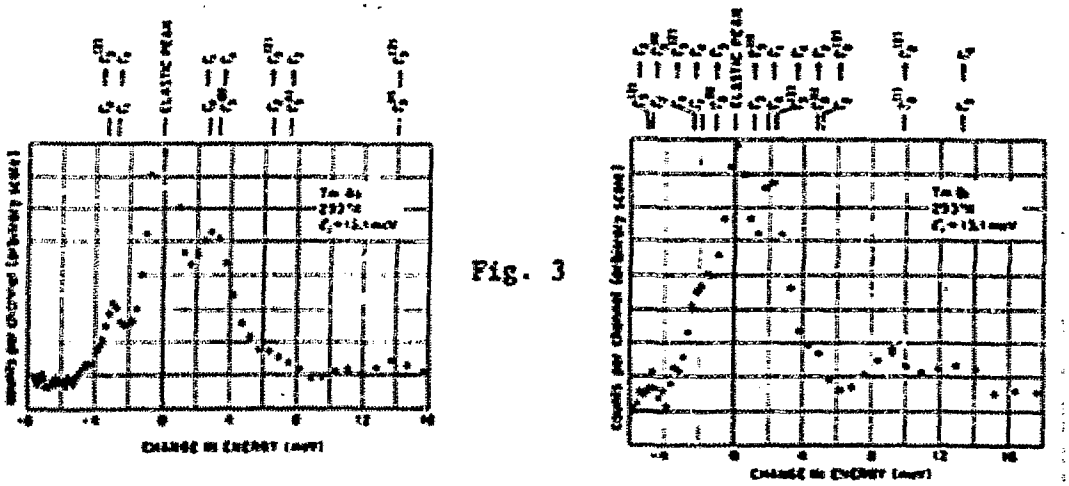

Fig. 3

of elastic peaks have been excluded from the experimental-calculated comparison.

The above procedures lead to fits of the TmAs and TmBi data with "goodness of fit" values, χ^2, less than 2.5 for all data sets. Parameters for the 78°K data are given in Table I, which also contains results for TmSb.[3] Although some temperature variation of the crystal-fields was observed, the analyses of 4.2 and 293°K data are consistent with the results of Table I. The quantities $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$ are related to W and x via $A_4\langle r^4\rangle\chi_4 F(4) = Wx$ and $A_6\langle r^6\rangle\chi_6 F(6) = W(1 - |x|)$, where χ_4 and χ_6 are reduced matrix elements.[6] The Z_i are effective charges used in a nearest-neighbor point-charge model to reproduce the empirical $A_i\langle r^i\rangle$. These Z_i were calculated using the relativistic matrix elements $\langle r^i\rangle^{++}$ as tabulated by Lewis.[12]

The charges Z_4 fall in the range 2 to 3, which might be expected from simple valency considerations. Thus, a simple point-charge model has reasonable success in accounting for some features of the crystal-fields for these compounds. We do not understand the reasons for this partial success and it is puzzling if one considers, as discussed by Turberfield et al.,[2] mechanisms expected to make a point-charge model inoperative in metallic compounds. The Z_6 values are considerably larger than expected from valency considerations, which is perhaps pleasing since they may reflect some of the complications expected in metallic systems. However, as discussed by Birgeneau et al.,[3] a large Z_6/Z_4 ratio is commonly found in insulators and usually ascribed to overlap and covalency effects. A large Z_6/Z_4 ratio for the TmX compounds is strange when contrasted with the approximately unity values found[2,5] for all PrX compounds. Although this difference in ratio has been commented on before,[3] our results reinforce its occurrence and indicate it will probably occur between all metallic PrX and TmX compounds. Whether or not it occurs between the semiconducting PrN and TmN remains open, and an investigation of TmN could provide some clue for its occurrence.

The $A_4\langle r^4\rangle$ values of Table I follow the trend required to make an approximate linear correlation between them and the electronegativity of the ligands, as has been pointed out for PrX[7,8] and NdX[8] compounds. However, due to the rather minor variation in electronegativity

between As, Sb, and Bi (about 2.0 to 1.8) and the errors associated with the $A_4\langle r^4\rangle$ values, we do not believe that the values of Table I establish a definite correlation for TmX compounds. It would be helpful to have available $A_4\langle r^4\rangle$ values for TmP and TmN before attempting to establish any correlation with electronegativity. Since N has an electronegativity of about 3, work on TmN would be especially useful. Because neutron work on TmN could possibly illuminate both this aspect and the Z_6/Z_4 ratio question, we presently are investigating this compound.

TABLE I. Parameters derived from 78°K neutron data.

	TmAs	TmSb	TmBi
x	- 0.79 ± .02	- 0.785 ± .02	- 0.81 ± .03
W (meV)	- 0.106 ± .002	- .00856 ± .002	- 0.0736 ± .0025
$A_4\langle r^4\rangle$ (meV)	8.55 ± .15	6.81 ± .10	6.09 ± .15
$A_6\langle r^6\rangle$ (meV)	0.53 ± .06	0.44 ± .04	0.33 ± .07
a (Å)	5.711	6.084	6.192
Z_4	2.05	2.26	2.19
Z_6	7.01	9.04	7.77

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