PHYSICAL REVIEW B VOLUME 36, NUMBER 1 1 JULY 1987

Anisotropic magnetic properties of single crystals of $SmRh_4B_4$

H. Zhou, S. E. Lambert,* and M. B. Maple
Department of Physics and Institute for Pure and Applied Physical Sciences, University of California, San Diego, La Jolla, California 92093

S. K. Malik† and B. D. Dunlap
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 17 December 1986)

The magnetic susceptibility of single crystals of $SmRh_4B_4$ has been measured for two orientations of the crystals with respect to the applied field H. At low temperatures, the easy direction of magnetization is perpendicular to the tetragonal c axis, while for temperatures higher than 73 K, the easy axis of magnetization is parallel to the c axis. The data have been analyzed by including intermediate coupling of the lowest three J manifolds of the Sm^{3+} ion, crystal-field interactions, and conduction-electron polarization effects. The anisotropy crossover is shown to result primarily from a competition between the anisotropy of the crystal-field energy levels in the ground ($J=\frac{5}{2}$) manifold and the anisotropy of Van Vleck terms due to mixing of the $J=\frac{5}{2}$ and $J=\frac{7}{2}$ manifolds.

INTRODUCTION

The interplay of superconductivity and long-range magnetic order has been studied extensively in the primitive tetragonal rare-earth rhodium boride compounds RRh_4B_4.[1] One of the three members of this family that exhibit the coexistence of superconductivity and long-range antiferromagnetic order is the compound $SmRh_4B_4$, which has a superconducting transition temperature (T_c) of 2.7 K and a Néel temperature (T_N) of 0.87 K.[1-2] Recently, we prepared single crystals of this compound[3,4] and investigated their magnetic properties with special emphasis on magnetic anisotropy, the results of which are reported herein. The data are well described by a theoretical calculation which includes the influence of the crystalline electric field[5] (CEF) and conduction-electron polarization effects.[6]

EXPERIMENTAL DETAILS

The samples were prepared by precipitation from a flux of molten copper using a technique reported by Takei *et al.*,[7] although we used a crucible made of ThO_2 rather than Al_2O_3. The crystals are rectangular parallelepipeds with dimensions $\sim 0.3\times 0.3\times 5$ mm^3 where the tetragonal c axis coincides with the long axis of the samples. A metallographic examination revealed that some crystals contain inclusions of copper estimated to be 5–10 % by volume, and inclusions of RhB may also be present. The dc magnetization susceptibility χ was determined in a superconducting quantum-interference device magnetometer with an applied field of 10 kG for temperatures 2 $K \leq T \leq 300$ K. A thin sapphire plate was used as a sample holder whose diamagnetic background was compensated by a small spiral of high-purity Pt wire. Approximately 20 crystals with total mass ~ 9 mg were glued to the plate with the c axis of the various crystals coincident within an error estimated to be 5°. An effort was made to place one of the a axes perpendicular to the surface of the sapphire, but this was difficult due to irregular projections from the surfaces of the crystals. The sapphire plate was then glued to a 12-cm thin quartz tube which was attached with thread to the sample hook of the magnetometer. The sapphire plate could be unglued and rotated without disturbing the arrangement of the crystals, permitting the magnetic anisotropy to be determined. Rotation of the sample assembly was limited to $\pm 1.5°$ in the sample tube of the magnetometer. Measurement of various collections of crystals gave results in good agreement with one another. The typical sample-holder contribution to the total signal ranged from 13% (15%) at $T=300$ K to 19% (6%) at $T=2$ K with the c-axis oriented parallel (perpendicular) to the applied field H.

RESULTS

Displayed in Fig. 1 is the temperature dependence of χ^{-1} for single crystals of $SmRh_4B_4$ oriented with the c axis either parallel or perpendicular to the applied magnetic field. The error bars represent estimates of the uncertainty due to subtraction of the sample-holder background. The unknown content of inclusions and impurities in our crystals makes it difficult to calculate reliably the molar susceptibility. Consequently, we have estimated a polycrystalline average from the single-crystal data using $\chi_{av}=\chi_{\parallel}/3+2\chi_{\perp}/3$, which is also shown in Fig. 1, where $\chi_{\parallel}$ ($\chi_{\perp}$) is the component of χ that is parallel (perpendicular) to the c axis. This estimate of χ_{av} is in good agreement with the previously measured data[2] for a polycrystalline sample of $SmRh_4B_4$ if it is multiplied by a scaling factor of 1.43. The ordinate in Fig. 1 reflects the molar susceptibility of the polycrystalline sample. These values should be viewed with some caution since the scale would be affected by impurity phases and by preferred

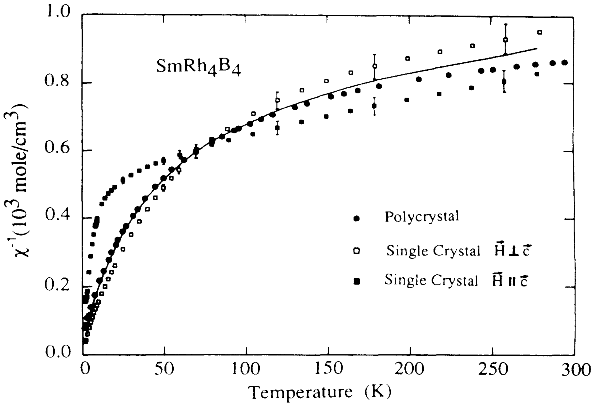

FIG. 1. The inverse magnetic susceptibility χ^{-1} vs temperature T for single crystals of SmRh$_4$B$_4$ oriented with the c axis either parallel (||) or perpendicular ($\perp$) to the applied magnetic field H. Also shown by the solid line is a polycrystalline average of these data, calculated as described in the text, and previous data measured on a polycrystalline sample (Ref. 2). The $\chi(T)$ data for the single crystals have been multiplied by 1.43 to obtain agreement with the polycrystalline data. The error bars show the estimated experimental uncertainty due to subtraction of the sample holder background. See text for details.

orientation of the crystallites in the polycrystalline sample. Data for a polycrystalline sample of the nonmagnetic, isostructural compound LuRh$_4$B$_4$ (Ref. 8) are at most 5% of the values for polycrystalline SmRh$_4$B$_4$ in the temperature range investigated, indicating that the non-4f contribution to the magnetic susceptibility is negligible. A noteworthy feature of these data is the reversal of magnetic anisotropy observed for $T\approx 73$. At low temperatures, the easy axis of magnetization is perpendicular to the c axis, while for $T>73$ K, the easy axis is parallel to the c axis.

ANALYSIS

Previous work[2] has shown that $\chi(T)$ for polycrystalline SmRh$_4$B$_4$ can be described by the equation

$$\chi=[\mu_{\text{eff}}^2/3(T-\Theta)+\mu_B^2/\delta]N_A/k_B\ , \tag{1}$$

where μ_{eff} is the effective magnetic moment, Θ is the Curie-Weiss temperature, μ_B is the Bohr magneton, δ is an energy scale defined below, N_A is Avogadro's number, and k_B is Boltzmann's constant. The first term represents the Curie-Weiss susceptibility from the ground-state energy levels with total angular momentum $J=\frac{5}{2}$, while the second term is a temperature-independent Van Vleck susceptibility due to coupling with the $J=\frac{7}{2}$ multiplet at an energy ΔE above the ground state, where $\delta=7\Delta E/20$. The Van Vleck susceptibility is very important for Sm^{3+} ions due to the small magnitude of μ_{eff}, the rather low value of $\Delta E(\sim 1400$ K), and the relatively large matrix elements coupling the $J=\frac{5}{2}$ and $J=\frac{7}{2}$ energy levels. These polycrystalline data for SmRh$_4$B$_4$ were subsequently reanalyzed to include conduction-electron polarization effects, which can be large for Sm^{3+} compounds.[9] However, no attempt was made to include crystalline electric field (CEF) effects in the calculations.

Inclusion of CEF terms considerably complicates the analysis because of the introduction of magnetic anisotropy. This is more difficult for Sm than for other rare-earth metals since the anisotropy will be reflected not only in the values of magnetic moments within a given J multiplet, but also in the Van Vleck–type contributions to the magnetic susceptibility and in the conduction-electron polarization effects. We have therefore employed a numerical procedure which treats all energy terms on an equal basis, using procedures described elsewhere.[10,11] Taking a Hamiltonian

$$\mathcal{H}=\lambda\mathbf{L}\cdot\mathbf{S}+\mathcal{H}_{\text{CEF}}+\mu_B H(L_z+2S_z)\ , \tag{2}$$

where $\mathcal{H}_{\text{CEF}}$ describes the crystal-field interactions,[5] an energy matrix is calculated which includes the mixing between J manifolds by the various interactions. Thus CEF interactions are included not only in the $J=\frac{5}{2}$ and $J=\frac{7}{2}$ multiplets, but also when finite matrix elements couple the two.[10] Since J is not a good quantum number in this case, the magnetic moment is taken to be proportional to L_z+2S_z. The spin-orbit parameter has been given a typical value, $\lambda=410$ K. The energy matrix was diagonalized using the three lowest J multiplets, to obtain the energy levels and eigenvectors. Neglecting the higher multiplets, situated at >5000 K above the ground state, introduces no significant error. The susceptibility for a given temperature was obtained by evaluating the magnetic moment, $\mu=-\langle L_z+2S_z\rangle\mu_B$ for each level, performing a thermal average to obtain the magnetization M, and numerically calculating $\chi=M/H$. In such a procedure, where the Zeeman interaction is not treated as a perturbation but as an integral part of the diagonalized Hamiltonian, the Van Vleck contributions to the susceptibility appear automatically. In this way, one obtains the susceptibility $\chi_0(T)$ for a given set of CEF parameters. In the present calculation, we have used CEF parameters previously obtained and successfully used to describe many of the properties of the RRh$_4$B$_4$ compounds.[5,12]

For direct comparison to the data, we have used the expression[6]

$$\chi=\frac{\chi_0\left[1+\alpha\dfrac{\langle S_z\rangle}{\langle L_z+2S_z\rangle}\right]}{1-\gamma\chi_0}\ . \tag{3}$$

The term containing α gives a correction for conduction-electron polarization. The term with γ is a correction for exchange interactions. Both α and γ are assumed to be isotropic, while χ_0 and $\langle S_z\rangle$ depend on the orientation of the magnetic field with respect to crystalline axes. The factor γ has been obtained in the mean-field approximation for this antiferromagnetic material as

$$\gamma=-1/\chi_0(T_N)\ , \tag{4}$$

where $T_N=0.87$ is the antiferromagnetic transition temperature. The calculated susceptibility is again multiplied by a temperature-independent scaling factor to account for nonmagnetic impurities in the sample. This factor was determined by requiring calculated and experimental values of the polycrystalline average $(\chi_{\parallel}/3+2\chi_{\perp}/3)$ to be equal at $T=80$ K.

Equation (3) was used in a least-squares program to obtain best fits to the data. Since the CEF parameters are known, γ is determined directly by calculation. The scale factor is determined for a given set of parameters by direct comparison with the data. Therefore, the only fitting parameter is the spin-polarization factor, α. However, consideration has been given to a possible misalignment of the sample, particularly for the hard axis, due to a tendency of the sample to rotate in the magnetometer toward the easy axis. We assume a temperature-independent misorientation for these calculations, although this is probably a poor approximation since the anisotropy is strongly temperature dependent. The solid lines in Fig. 2 show the results of the fit, taking the magnetic field along the a axis for $\chi_{\perp}$ and at 10° to the c axis for $\chi_{\parallel}$. In view of the experimental error bars and uncertainty as to the nature of any impurity phases present, the fit is seen to give a very good representation of the data.

It should be noted that the effect of exchange interactions is small due to the low value of T_N, but inclusion of conduction-electron polarization effects is important for describing the data in both orientations.[6,9] This is demonstrated in Fig. 2 where the dashed lines give the results of a calculation using the same parameters as the solid lines, but with $\alpha=0$. The value obtained from the best fit, $\alpha=0.064$, is significantly larger than the value of 0.022 obtained by Stewart from an analysis of the polycrystalline data, ignoring CEF effects.[9] As Stewart has noted, α is given by

$$\alpha=2\mathscr{J}N(0)\ , \tag{5}$$

where $\mathscr{J}$ is the exchange coupling between the spin $\mathbf{S}$ of a local moment and the spin $\mathbf{s}$ of a conduction electron in the Hamiltonian $H_{\text{ex}}=-2\mathscr{J}\mathbf{S}\cdot\mathbf{s}$, and $N(0)$ is the density of states per spin direction at the Fermi level. If we use the value calculated for ErRh_4B_4, $N(0)=0.35$ states/(atom)(spin direction),[13] we then obtain $\mathscr{J}=0.09$ eV. This is substantially larger than that obtained by other estimates[14-15] and, furthermore, is incompatible with the value of $N(0)\mathscr{J}^2=3.4\times10^{-4}$ eV obtained by analysis of superconducting transition temperatures.[16] Thus, while the above clearly demonstrates the importance of including conduction electron polarization in the susceptibility analysis, it is likely that the magnitude has been overestimated here, perhaps because of the way in which the impurity phases have been treated in the analysis.

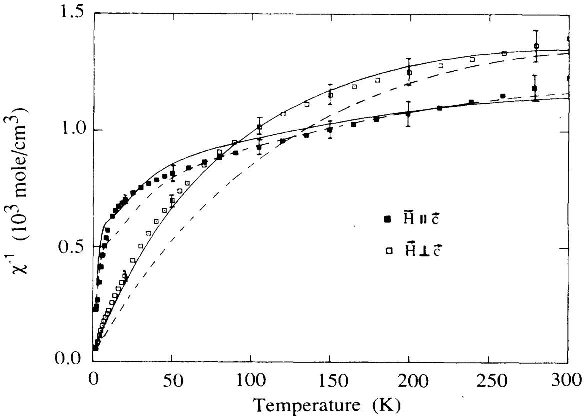

FIG. 2. The calculated inverse magnetic susceptibility χ^{-1} vs temperature for SmRh_4B_4 oriented with the c axis either parallel ($\parallel$) or perpendicular ($\perp$) to the applied magnetic field H. The calculated results have been multiplied by 1.36. The dashed lines show the effect of neglecting conduction electron polarization in the analysis.

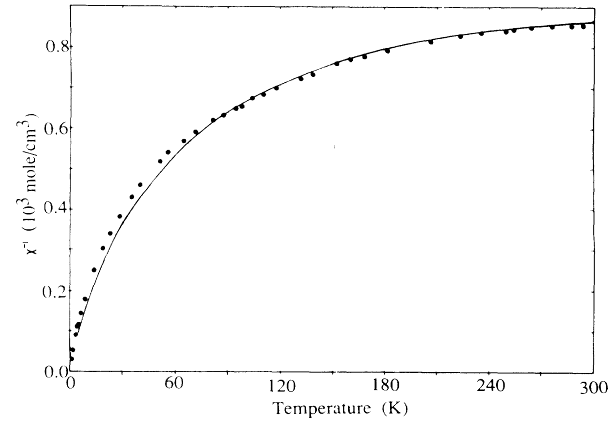

FIG. 3. Comparison of the calculated susceptibility $\chi_{\text{av}}=\chi_{\parallel}/3+2\chi_{\perp}/3$ (solid lines), with polycrystalline data (Ref. 2) for SmRh_4B_4 (solid circles). The calculated results have been multiplied by 1.09.

The factor scaling the overall magnitude of the susceptibility obtained from the fit of Fig. 2 has the value 1.36, somewhat smaller than that of 1.43 obtained from the comparison of Fig. 1. This indicates that impurity phases also affected the molar susceptibility determined from the previous polycrystalline data. This can be verified by comparing the calculated polycrystalline susceptibility with the data of Ref. 2. Figure 3 demonstrates that such a calculation reproduces the polycrystalline molar susceptibility extremely well over the entire temperature range, provided the calculated values are scaled by a factor of 1.09.

DISCUSSION

The analysis described above represents the first case in which the magnetic susceptibility of a Sm compound has been analyzed including (a) crystal-field splittings, (b) intermediate coupling of the J states, (c) exchange corrections (within the mean-field approximation), (d) Van Vleck contributions between the J levels, (e) conduction-electron polarization, and (f) thermal population of the excited J levels. In the present case, (c) and (f) do not make major contributions, but all of the other factors must be included to arrive at an adequate description of the data.

The most striking feature of the data for $SmRh_4B_4$ is the crossover in magnetic anisotropy that occurs between high and low temperatures. Such changes have been observed previously in magnetically ordered materials,[17–18] but the observation in a paramagnetic material clearly requires single-crystal data such as those presented here. The origin of the anisotropy crossover in the present case can be understood as a competition between the crystal-field-induced anisotropy and anisotropy in the Van Vleck contributions. Consider a simplified case in which the CEF interaction contains only the axial term $B_2^0[3J_z^2-J(J+1)]$. If $B_2^0>0$, the system will have its magnetic easy axis in the basal plane ($\chi_\perp>\chi_\parallel$) at low temperatures. At higher temperatures, the Van Vleck terms must be included. These are given by[19]

$$\chi_i^V=\frac{N_A\mu_B^2}{k\Delta E}\sum_n \chi_{n,i}^V e^{-E_n/kT} , \tag{6}$$

where

$$\chi_{n,i}^V=2\sum_{n'} |\langle n|L_i+2S_i|n'\rangle|^2 . \tag{7}$$

Here, $|n\rangle$ and $|n'\rangle$ denote the CEF levels of the $J=\frac{5}{2}$ and $J'=\frac{7}{2}$ manifolds, respectively, and $i=x$ and z for $\chi_\perp$ and $\chi_\parallel$, respectively. For this simple CEF interaction, the wave functions are Kramers doublets of the form $|\pm J_z\rangle$, where $J_z=\frac{1}{2},\frac{3}{2}$, and $\frac{5}{2}$ in the ground-state manifold and $\frac{1}{2},\frac{3}{2},\frac{5}{2}$, and $\frac{7}{2}$ in the excited-state manifold. Direct calculation using the appropriate matrix elements coupling the two J manifolds[20] gives the contributions to the Van Vleck susceptibility from each of the CEF doublets, displayed in Table I. At very high temperatures where all of the $J=\frac{5}{2}$ CEF states are equally occupied with a population of $1/(2J+1)$, a susceptibility contribution of $20N_A\mu_B^2/7k\Delta E$ is obtained in both directions. However, at temperatures where the $|\pm\frac{5}{2}\rangle$ level is weakly occupied, Table I shows that $\chi_\parallel^V>\chi_\perp^V$. The Van Vleck terms dominate in the intermediate-temperature range, while the ground manifold CEF terms dominate at low temperatures. Since these two contributions have opposite anisotropy, a crossover is observed. By this argument, one expects the crossover to be a general feature for compounds having $\chi_\perp>\chi_\parallel$ at low temperatures, while the crossover should not be expected to occur if the system has $\chi_\parallel>\chi_\perp$ at low temperatures.

TABLE I. Calculated values of Van Vleck susceptibility contributions from the CEF levels of a ground $J=\frac{5}{2}$ manifold and excited $J=\frac{7}{2}$ manifold, assuming axial symmetry.

$\|n\rangle$	$\chi_{n,\parallel}^V$	$\chi_{n,\perp}^V$
$\|\pm\frac{1}{2}\rangle$	$\frac{360}{49}$	$\frac{240}{49}$
$\|\pm\frac{3}{2}\rangle$	$\frac{300}{49}$	$\frac{270}{49}$
$\|\pm\frac{5}{2}\rangle$	$\frac{180}{49}$	$\frac{330}{49}$

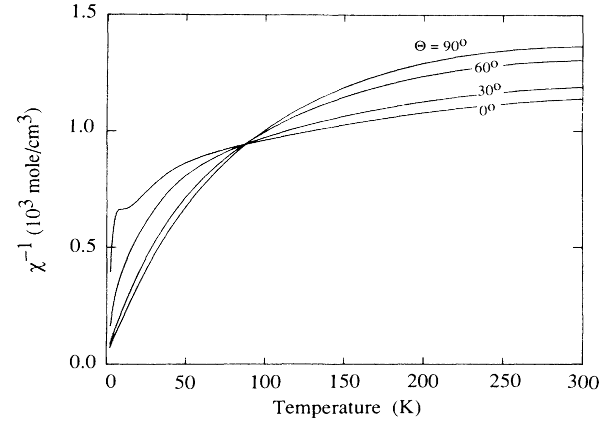

FIG. 4. Temperature dependence of χ for various orientations of $SmRh_4B_4$, calculated with parameters given in the text. The parameter θ is the angle of the applied magnetic field with respect to the tetragonal c axis.

In $SmRh_4B_4$, the CEF Hamiltonian is more complex than in this simple model, but these results can be used to estimate the high temperature anisotropy of that material. If we take the $|\pm\frac{3}{2}\rangle$ doublet at 22 K and the $|\pm\frac{5}{2}\rangle$ doublet at 190 K above the $|\pm\frac{1}{2}\rangle$ doublet, corresponding to the calculated CEF splitting for $SmRh_4B_4$, then the use of Eq. (6) and Table I gives $\chi_\parallel^V/\chi_\perp^V=1.1$ at 300 K. This should be compared with the experimental value of 1.14. In view of the approximate nature of the model, one should not overemphasize the good agreement, but this does indicate that the explanation of the high-temperature results in terms of an anisotropy in the Van Vleck susceptibility is correct.

Using the full Hamiltonian of Eq. (2), the temperature dependence of the susceptibility for various orientations of H with respect to the c axis has been calculated and is displayed in Fig. 4. An interesting aspect of the calculat-

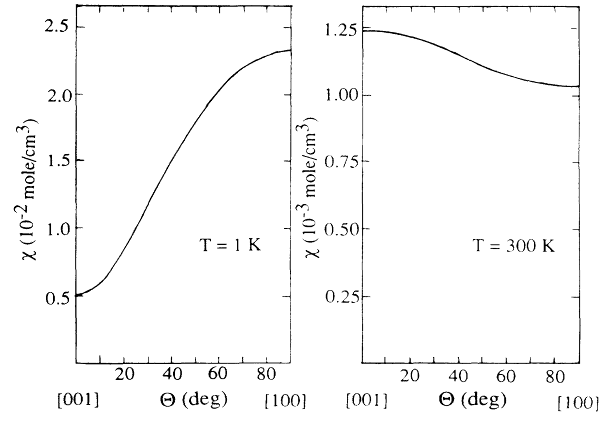

FIG. 5. Angular dependence of χ for $SmRh_4B_4$ at $T=1$ K and at $T=300$ K, calculated with parameters given in the text. The variable θ is the angle of the applied magnetic field with respect to the tetragonal c axis.

ed values for $\theta = 0°$ is the peak at ≈ 10 K, which occurs when the first excited CEF level of the $J = \frac{5}{2}$ multiplet, located at 22 K above the ground state, is populated. More detailed experiments in this temperature range are planned to confirm this feature. Finally, we display in Fig. 5 the results of calculating the variation of χ as the angle between the c axis and H is changed at low and high temperatures. This shows, in another fashion, the reversal of the anisotropy. In all cases, calculations show that the anisotropy in the basal plane is very small.

CONCLUSION

We have determined the magnetic susceptibility of the primitive tetragonal compound $SmRh_4B_4$ for two orientations with respect to the applied magnetic field. The easy direction of magnetization is perpendicular to the c axis at low temperatures and parallel to the c axis for temperatures higher than 73 K. This behavior is well reproduced by calculations of the susceptibility including mixing of energy levels with total angular momentum $J = \frac{7}{2}$ into the ground state with $J = \frac{5}{2}$, the influence of the crystalline electric field, and conduction-electron polarization through the exchange interaction.

ACKNOWLEDGMENTS

This research was supported by the U. S. Department of Energy, under Grant No. DE-FG03-86ER45230 at UCSD and by the U. S. Department of Energy, BES-Materials Sciences, under Contract No. 31-109-ENG-38 at Argonne National Laboratory. One of us (M.B.M.) would like to express his appreciation to the John Simon Guggenheim Foundation for support while part of this work was being carried out.

---

[*] Present address: IBM Almaden Research Center, San Jose, CA 95120.

[†] Permanent address: Tata Institute of Fundamental Research, Bombay, India.

[1] M. B. Maple, H. C. Hamaker, and L. D. Woolf in *Superconductivity in Ternary Compounds II*, Vol. 34 of *Topics in Current Physics*, edited by M. B. Maple and Ø. Fischer (Springer-Verlag, New York, 1982).

[2] H. C. Hamaker, L. D. Woolf, H. B. MacKay, Z. Fisk, and M. B. Maple, Solid State Commun. **32**, 289 (1979).

[3] S. E. Lambert, H. Zhou, J. W. Chen, and M. B. Maple, Physica **135B**, 329 (1985).

[4] H. Zhou, J. W. Chen, S. E. Lambert, and M. B. Maple, J. Appl. Phys. **57**, 3115 (1985).

[5] B. D. Dunlap, L. N. Hall, F. Behroozi, G. W. Crabtree, and D. Niarchos, Phys. Rev. B **29**, 6244 (1984).

[6] A. M. Stewart, Phys. Rev. B **6**, 1985 (1972).

[7] H. Takei, T. Shishido, H. Iwasaki, and Y. Muto, Jpn. J. Appl. Phys. **22**, 1463 (1983).

[8] L. D. Woolf, D. C. Johnston, H. B. MacKay, R. W. McCallum, and M. B. Maple, J. Low Temp. Phys. **35**, 651 (1979).

[9] A. M. Stewart, Phys. Rev. B **24**, 4080 (1981).

[10] S. K. Malik, R. Vijayaraghavan, S. K. Garg, and R. J. Ripmeester, Pure Appl. Chem. **40**, 223 (1974).

[11] H. W. DeWijn, A. M. van Diepen, and K. H. J. Buschow, Phys. Rev. B **7**, 524 (1973).

[12] S. E. Lambert, M. B. Maple, and B. D. Dunlap, Phys. Rev. B **33**, 3129 (1986).

[13] T. Jarlborg, A. J. Freeman, and T. J. Watson-Yang, Phys. Rev. Lett. **39**, 1032 (1977).

[14] H. B. MacKay, L. D. Woolf, M. B. Maple, and D. C. Johnston, J. Low Temp. Phys. **41**, 639 (1980).

[15] G. K. Shenoy and S. K. Malik, Phys. Rev. B **33**, 6132 (1986).

[16] B. D. Dunlap, Phys. Rev. B **34**, 1469 (1986).

[17] U. Atzmony, M. P. Dariel, E. R. Bauminger, D. Lebenbaum, I. Nowik, and S. Ofer, in Proceedings of the Tenth Rare Earth Research Conference, Carefree, Arizona, 1973 (unpublished), p. 605.

[18] A. M. van Diepen, H. W. deWijn, and K. H. J. Buschow, Phys. Rev. B **8**, 1125 (1973).

[19] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

[20] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970), pp. 677–678.