

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

FINAL REPORT

to

The National Aeronautics and Space Administration

GRANT NO. NSG 3168

STUDIES OF MAGNETOSTRICTION AND SPIN POLARIZED BAND STRUCTURES

OF RARE EARTH INTERMETALLICS

(NASA-CR-158517) STUDIES OF
MAGNETOSTRICTION AND SPIN POLARIZED BAND
STRUCTURES OF RARE EARTH INTERMETALLICS
Final Report (Pittsburgh Univ., Pa.) 29 p
HC A03/MF A01

N79-22934

Unclas
25117

CSCI 20L G3/76

W. E. Wallace
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA. 15260

April, 1979



I. INTRODUCTION

The program submitted in October 1976 to NASA for support consisted of two rather distinct, albeit related parts. These were:

1. Study of Magnetostriction of Rare Earth Systems
2. Band Structure Calculations

It is appropriate to begin this report by indicating the rationale and scope of the work.

1. Magnetostriction Studies

The end objective of this phase of work was to advance the utility of rare earth systems as transducers and sensors for servomechanisms. The work was to involve:

- a. Measurement of the magnetostrictive coefficients (λ) for selected systems;
- b. examination of the measured values of λ in terms of the single ion crystal field model as applied to the rare earth sublattice;
- c. making appropriate elastic constant measurements.

This information was intended for use in constructing a framework to enable one

- d. to predict materials with exceptionally large λ values, and
- e. to permit the construction of a framework for optimizing a material for magnetostrictive applications by taking into account not only the magnitude of λ but also the constraints imposed by materials features, such as saturation magnetization, magnetic anisotropy, Curie temperature, processing economics, etc.

2. Band Structure Calculations

Band structures were to be calculated by the APW method

- a. on selected RCo_5 systems (R = a rare earth);
- b. on selected RNi_5 systems;
- c. on selected RFe_2 systems;
- d. on the hypothetical RFe_5 systems.

The results were to be made use of in efforts to

- e. ascertain whether it is possible to effect coupling reversal between the rare earth and Co moments in RCo_5 systems by varying the electron concentration;
- f. account for the large hydrogen absorptivity of compounds such as $LaNi_5$;
- g. account for the non-existence of RFe_5 systems and certain RFe_2 systems, e.g., $PrFe_2$ and $LaFe_2$.

II. SUMMARY OF THE CURRENT STATUS OF PROPOSED TASKS

Support was requested for a two-year period but was only granted for a year. Accordingly, many of the tasks were incomplete. Some of the tasks had not even been initiated when notice of termination was received. The status of the several tasks is indicated in this section.

Part 1

Task

- 1a Completed work on R_6Fe_{23} systems with $R = Tb, Dy, Ho$ and Er .
- 1b Completed for Er_6Fe_{23} , temperature dependence only. Estimated theoretical values for R_6Fe_{23} with $R = Tb, Dy$ and Ho .
- 1c Incomplete. Needed equipment constructed and calibrated.
- 1d Not initiated.
- 1e Not initiated.

Part 2

- 2a Calculations completed for $SmCo_5, YCo_5$ and $GdCo_5$.
- 2b Calculations completed for $LaNi_5$ and $GdNi_5$.
- 2c Not initiated.
- 2d Calculations on hypothetical $SmFe_5$ in progress.

- 2e The calculations show that d-d coupling R 4d with Co 3d) is considerably stronger than the s-d or s-f exchange and hence rules out the possibility of effecting coupling reversal by altering through alloying the s electron concentration.
- 2f Question not resolved. Must make calculations on hydrided LaNi₅. Work yet to be initiated.
- 2g Yet to be initiated.

III. DETAILS OF COMPLETED PORTIONS OF THE PROGRAM.

Part 1 - Study of Magnetostriction of Rare Earth Systems

This work has been written up for presentation at the Fourteenth Rare Earth Research Conference to be held in Fargo, N.D. in June, 1979. The following is an account of the work as it is to be presented. The work is authored by F. Pourarian, W. E. Wallace, S. G. Sankar and R. Obermyer.

ABSTRACT

Anisotropic magnetostriction measurements of R₆Fe₂₃, R = (Tb, Dy, Ho and Er) have been carried out from 77 K to room temperature. Magnetic fields up to 2.1 Tesla were applied. All the compounds exhibited large magnetostrictions at 77 K, the largest effect being obtained for Tb₆Fe₂₃. Saturation magnetostriction values λ_s for the compounds were determined at 77.4 K and room temperature. Results of the temperature dependence of magnetostriction for Er₆Fe₂₃ are in good agreement with Callen and Callen's single ion theory. Therefore, the main source of magnetostriction in this compound is the Er ion.

INTRODUCTION

The magnetic properties of rare earth (R) and transition (T) elements have been the subject of great interest (1). The compounds of formula R₆Fe₂₃ crystallize with cubic Th₆Mn₂₃ structure type (2). The

iron atoms occupy four nonequivalent lattice sites. From bulk magnetization measurements of Hilscher and Rais (3) on $\text{Er}_6\text{Fe}_{23}$ and Van der Goot and Buschow (4) on $\text{Dy}_6\text{Fe}_{23}$, it is evidenced that in these compounds the rare earth moments are coupled ferrimagnetically to the resultant of the iron moments below the magnetic ordering temperature. These experiments yielded a saturation moment at the iron atoms of approximately $\mu_{\text{Fe}} = 2 \mu_{\text{B}}$. In all cases the magnetic ordering temperatures determined by Salmons (5) were found to be well above room temperature.

In magnetic materials the magnetoelastic coupling arises from the strain dependence of the exchange interaction and the orbital interaction between a magnetic ion and the local crystalline electric field. Large magnetostriction values have been observed for the cubic Laves RFe_2 (6) and RCo_2 (7) compounds. In RFe_2 , the source of this huge magnetostrictive effect was established to arise from the single-ion anisotropy of R sublattice moments (6,8). This anisotropy has its origin in the interaction between the rare earth ion and the crystalline field generated by the surrounding ions. In this paper we present the first experimental results of magnetostrictive strains in the polycrystalline samples of $\text{Tb}_6\text{Fe}_{23}$, $\text{Dy}_6\text{Fe}_{23}$, $\text{Ho}_6\text{Fe}_{23}$ and $\text{Er}_6\text{Fe}_{23}$ over the temperature range 77-300 K. Some of these compounds, due to their large magnetostriction values, may have a considerable importance for technical applications.

EXPERIMENTAL PROCEDURE

The bulk samples were prepared by melting the constituents in an induction furnace in a water-cooled copper boat under an argon atmosphere. The purity of the constituents was 99.9% for rare earth metals and 99.99% for iron. The resultant buttons were then annealed under high vacuum at 1100°C for periods between two to six weeks. X-ray

analysis of the powder of the annealed samples obtained revealed the presence of a small amount of second phase. For the measurements, the samples were cut into cylinders 5 mm in diameter and 2 mm long.

Measurements of linear magnetostriction were made using electrical resistance strain gauges (Micromeasurements type WK-05-031DE-350) in an applied magnetic field of 2.1 Tesla. The strains were measured with the field applied in parallel and then perpendicular to the gauge. These two strains are denoted by λ_{\parallel} and λ_{\perp} . In all cases the measured strains were quite large. Hence errors due to form effect and magneto-resistance in the gauges were negligible.

RESULTS AND DISCUSSION

The linear magnetostriction for cubic crystals may be described in terms of the conventional magnetostriction,

$$\frac{\delta l}{l} = 3/2 \lambda_{100}(C_1 - 1/3) + 3 \lambda_{111} C_2,$$

where λ_{111} and λ_{100} are magnetostriction constants and C_1 , C_2 are constants related to the average directions of magnetization and measurements. In the case of polycrystalline materials in which the preferred domain or grain orientation is absent, the magnetostrictive strain at the saturation can be shown to take the form: $\lambda_s = 2/5 \lambda_{100} + 3/5 \lambda_{111}$. Our results of magnetostriction are presented in terms of $\lambda_t = \lambda_{\parallel} - \lambda_{\perp}$ and for true saturation this equals $3/2 \lambda_s$. The isotropic distribution of the domains in our polycrystalline sample below the magnetic ordering temperature was verified by performing the measurements in the direction parallel and perpendicular (cooling direction) to the plane of the disc of the samples. The strains observed for the two cases differed by approximately 2 to 3%, which is within the experimental errors.

The magnetostriction isotherms for the compounds studied well below the Curie point are shown in Figs. 1-4. Saturation values, λ_s determined at room temperature and 77.4 K were obtained from extrapolation of the high field region (> 1.4 Tesla) of the strain-field curves to $1/H = 0$, except for $\text{Ho}_6\text{Fe}_{23}$ and $\text{Er}_6\text{Fe}_{23}$ at 77.4 K, where λ_s values were defined at 2.1 Tesla. The results are given in Table 1.

Table 1

Saturation Magnetostriction (λ_s) of Some
 R_6Fe_{23} Compounds

Compound	$10^6 \lambda_s (=2/3 \lambda_t)$	
	295 K	77.4 K
$\text{Tb}_6\text{Fe}_{23}$	633	2130
$\text{Dy}_6\text{Fe}_{23}$	293	240
$\text{Ho}_6\text{Fe}_{23}$	60 ^a	137 ^a
$\text{Er}_6\text{Fe}_{23}$	- 43 ^a	- 230

a. Values determined at 2.1 Tesla.
Other values obtained by extrapolation
to $1/H = 0$.

Among all the compounds studied, the highest magnetostriction was observed for $\text{Tb}_6\text{Fe}_{23}$. The lack of saturation of strains observed at maximum field of 2.1 Tesla (Fig. 1) indicates that this compound is highly anisotropic. The temperature variation of λ_t is shown in Fig. 5. The strain value resulting from extrapolation to $1/H = 0$ at 77.4 K is much larger than the value determined at 2.1 Tesla, at the same temperature. This implied that fields of the order of tens of Tesla will be needed to produce saturation at 77.4 K (or at 4.2 K).

Similar to the case of $\text{Tb}_6\text{Fe}_{23}$, the λ_t -H curves for $\text{Dy}_6\text{Fe}_{23}$ do not show saturation up to maximum applied fields (Fig. 2). A remarkable decrease in the magnitude of the strain at 2.1 Tesla below about 235 K was observed for this material (Fig. 6). Magnetization measurements which were reported previously (4) indicated that the compound

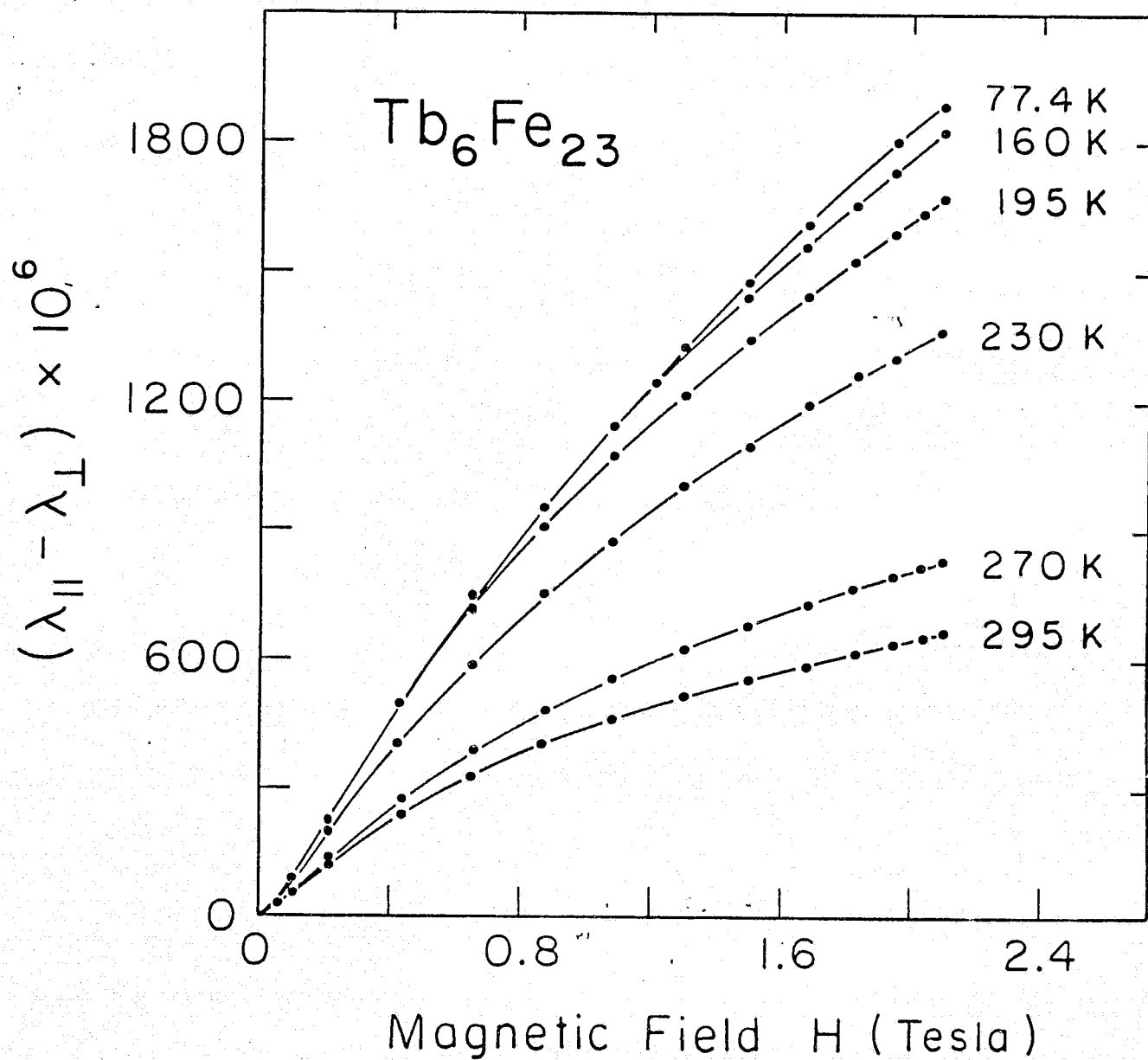


Fig. 1 Magnetostriction isotherm for Tb_6Fe_{23} .

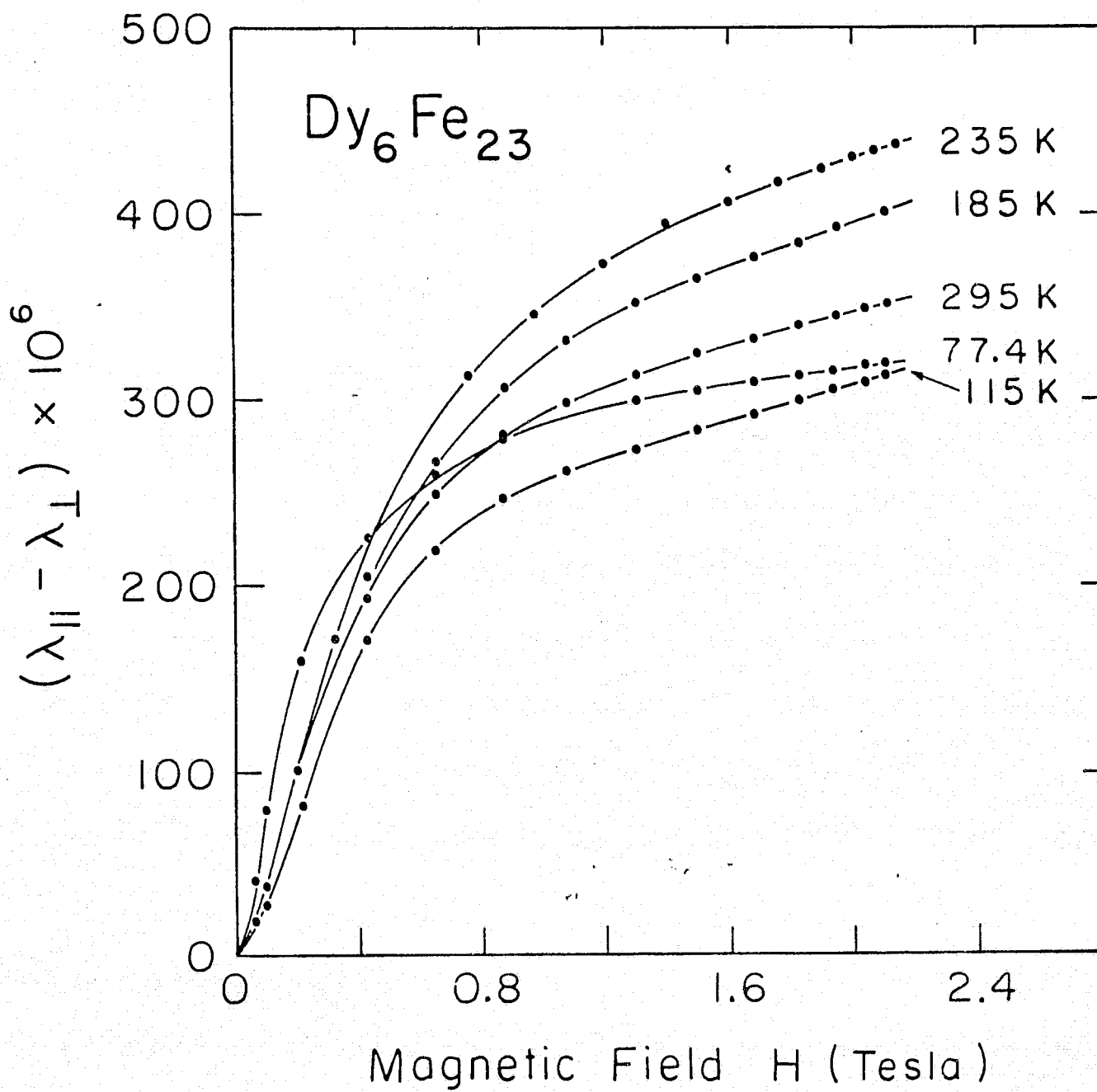


Fig. 2 Magnetostriction isotherm for $\text{Dy}_6\text{Fe}_{23}$.

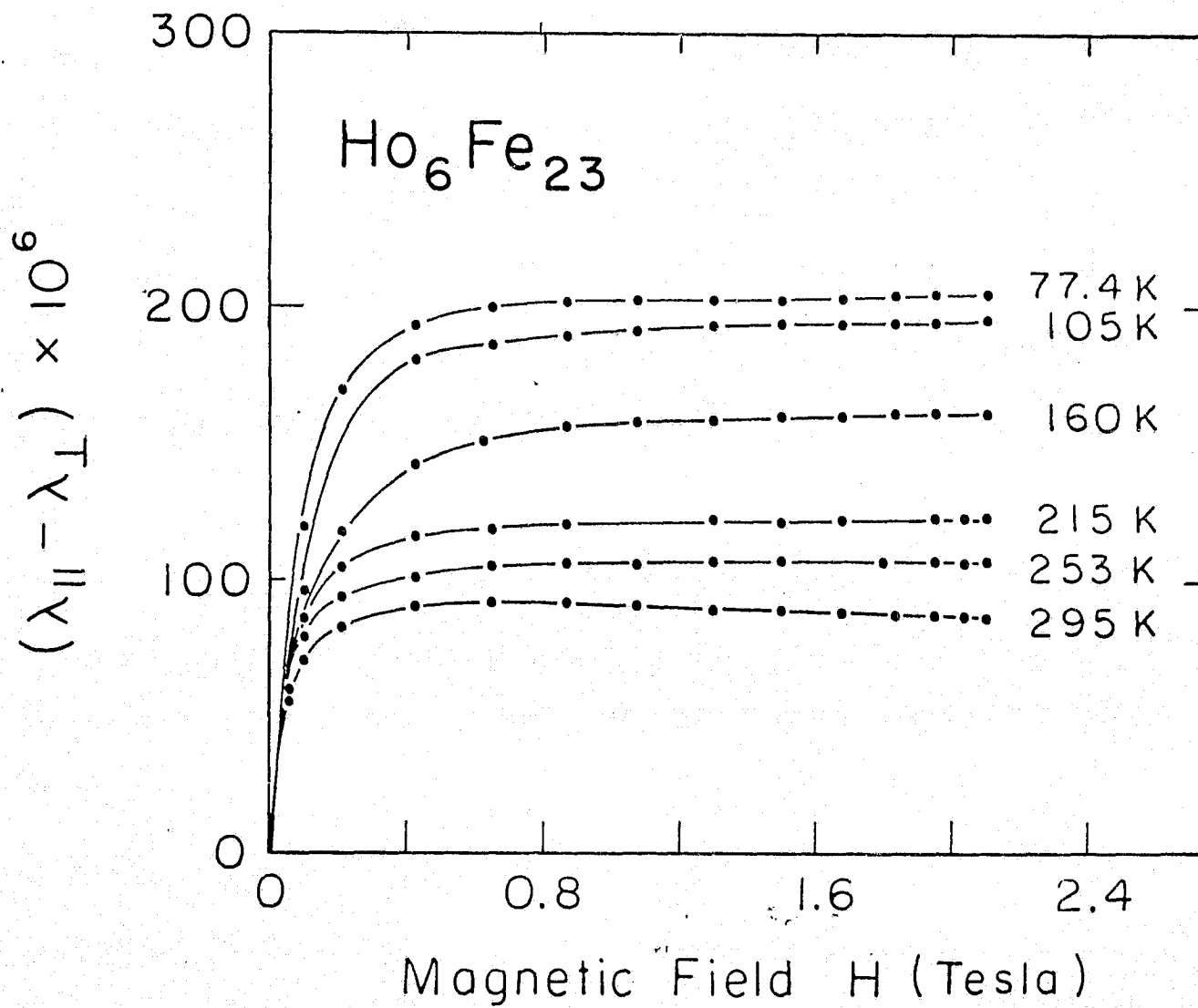


Fig. 3 Magnetostriction isotherms for $\text{Ho}_6\text{Fe}_{23}$.

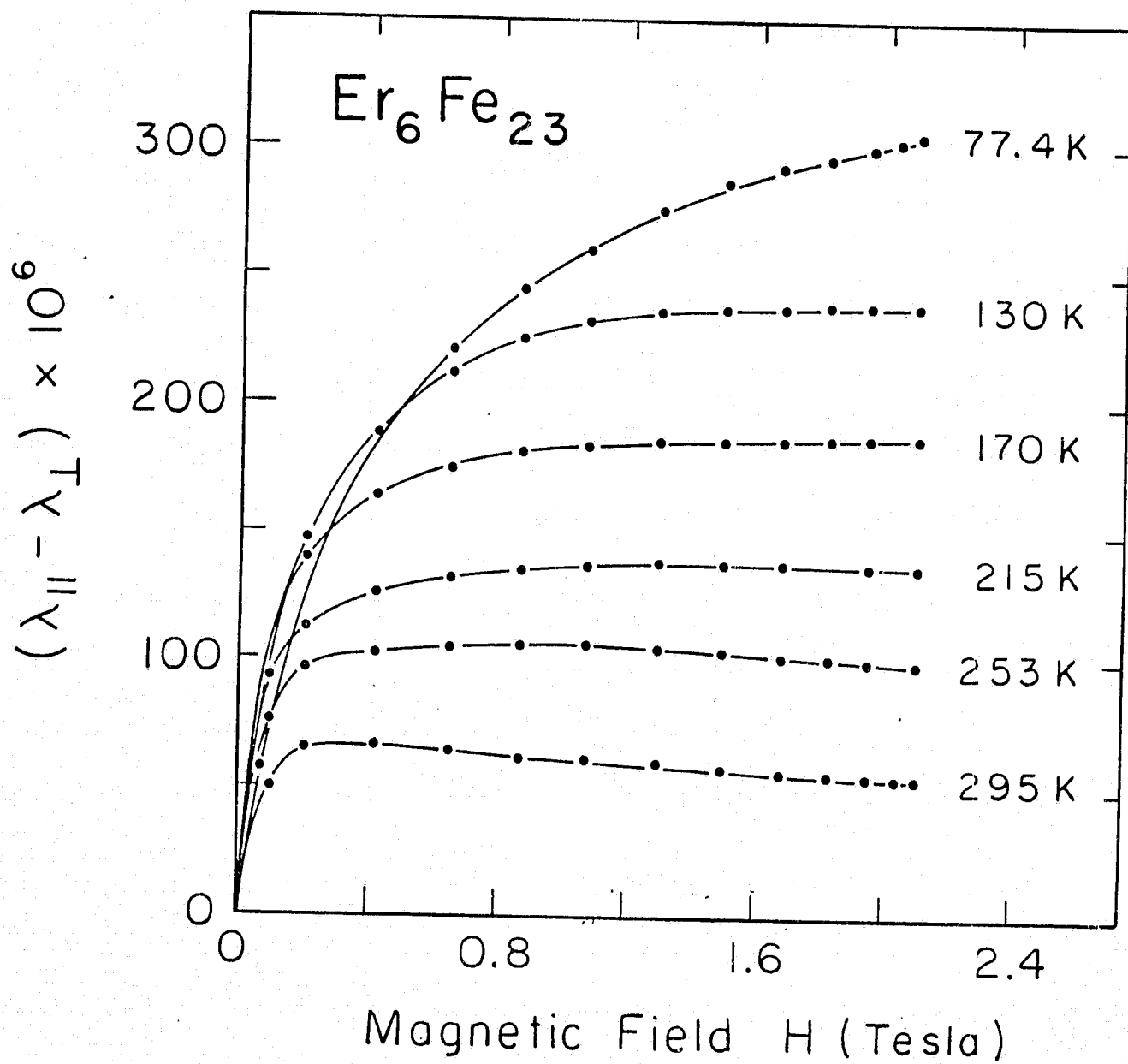


Fig. 4 Magnetostriction isotherm for $\text{Er}_6\text{Fe}_{23}$

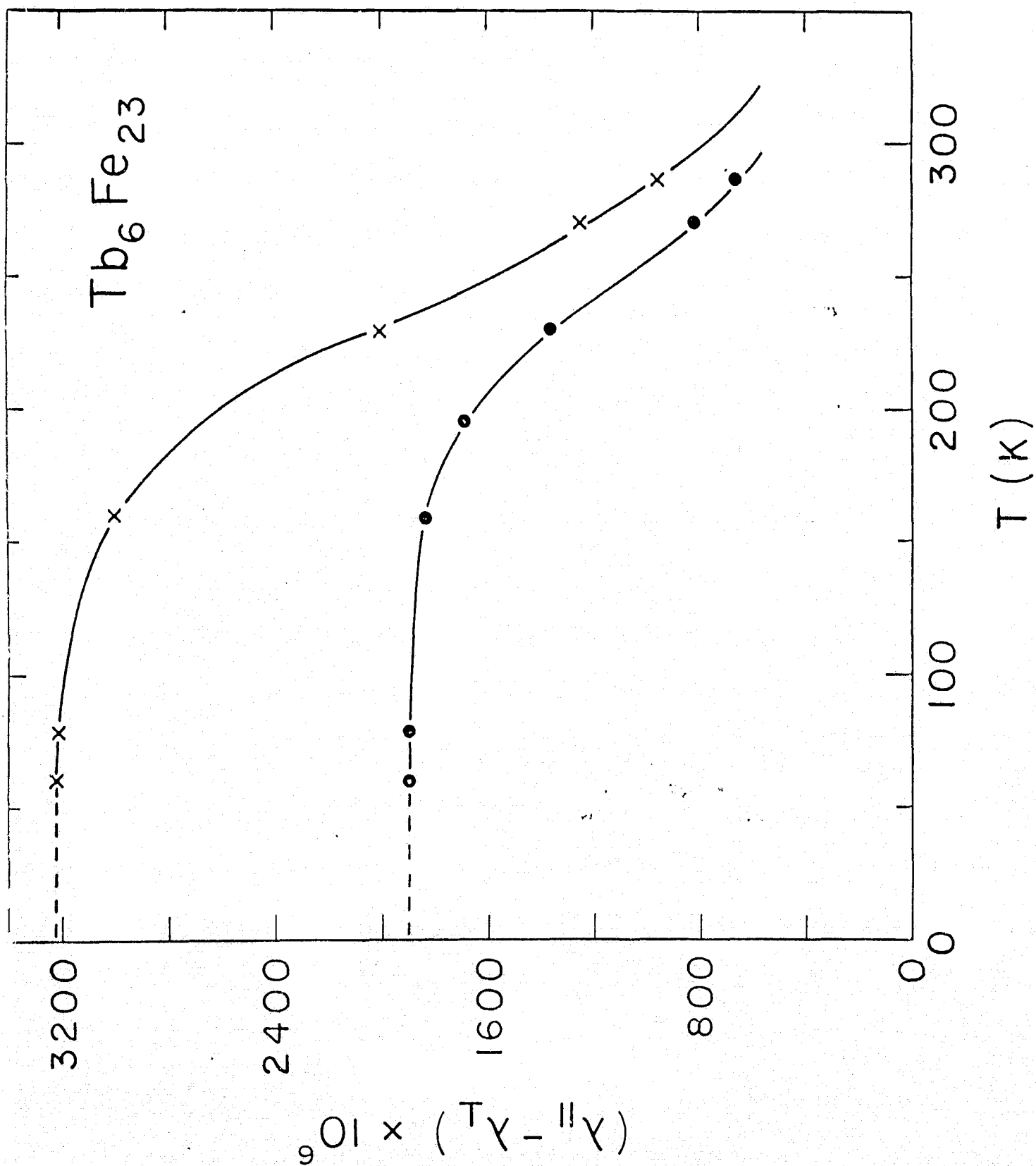


Fig. 5 Temperature dependence of $\lambda_{\parallel} - \lambda_{\perp} (= \lambda_T)$ for Tb_6Fe_{23} . Measured value at 2.1 Tesla (\bullet) and extrapolated value to $1/H = 0$ (\times).

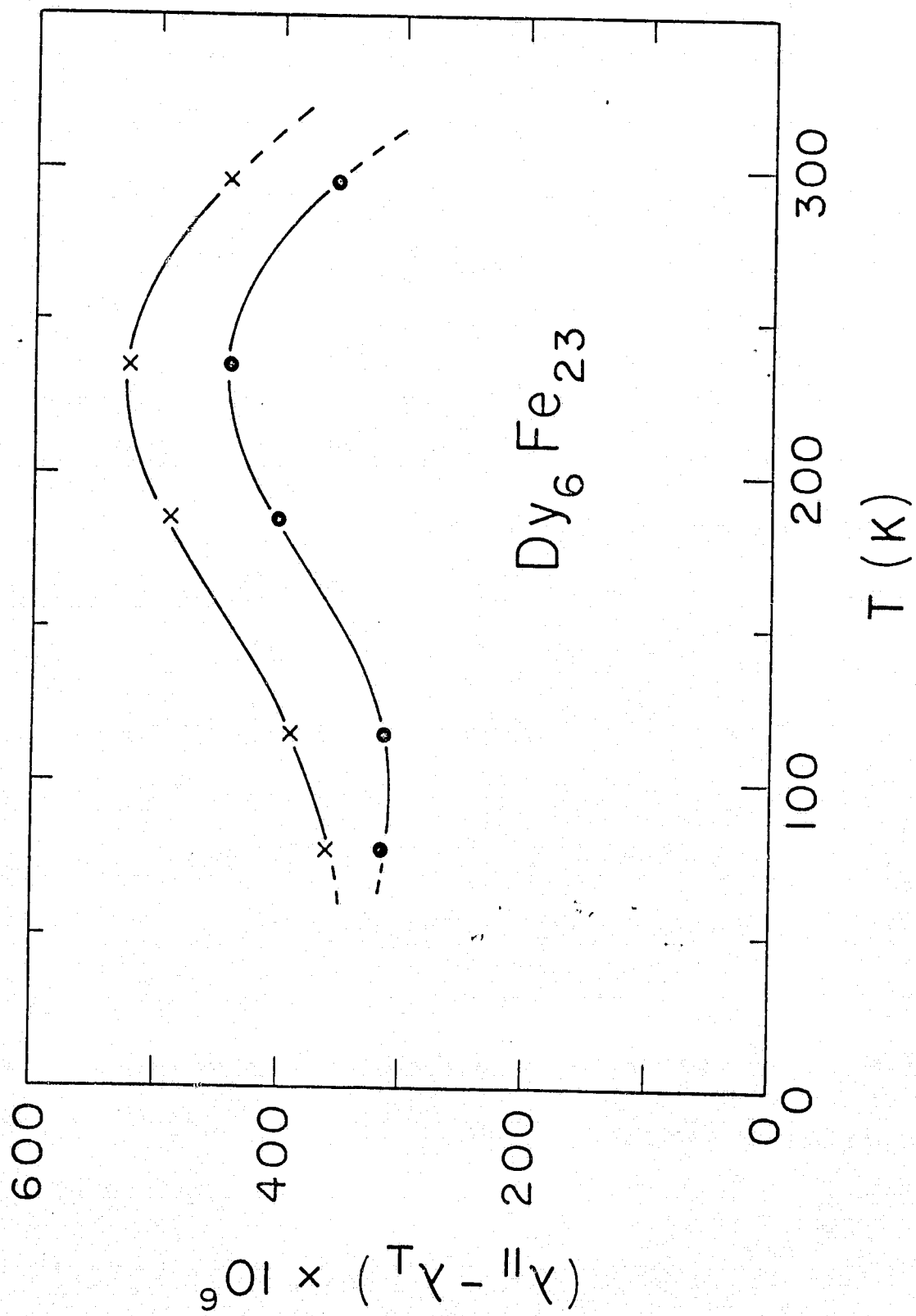


Fig. 6 Temperature dependence of $\lambda_{11} - \lambda_{1t} (= \lambda_t)$ for Dy_6Fe_{23} . Measured value at 2.1 Tesla (●) and extrapolated to $1/H = 0$ (x).

exhibited a compensation point at about 265 K, where the magnetization shows a minima. The reduction in strain suggests a rather strong increase in the anisotropy energy of the compound below the compensation point.

In the case of $\text{Ho}_6\text{Fe}_{23}$, the strain-field curves all appear to saturate at about 0.8 Tesla (Fig. 3). The temperature dependence of λ_t at saturation exhibited a normal behaviour (Fig. 7). Extrapolation of this curve below 77.4 K yielded a value of 237×10^{-6} at 0 K.

A large volume magnetostriction $\frac{\Delta V}{V} (= \lambda_{\parallel} + 2\lambda_{\perp})$ was obtained for $\text{Ho}_6\text{Fe}_{23}$ at all temperature ranges. This amounted to maximum values of about 65×10^{-6} and 100×10^{-6} at room temperature and 77.4 K, respectively. The volume strain is attributed to the rotation of the magnetization against the crystal anisotropy. It is interesting that the calculated values which are of the same order of magnitude as their relative strains (λ_t) indicate that the anisotropy energy is strongly volume-dependent.

For $\text{Er}_6\text{Fe}_{23}$, the magnetostriction isotherm curves exhibited saturation above 130 K (Fig. 4). At 77.4 K saturation of strains was not observed up to an applied field of 2.1 Tesla. Results of temperature dependence of magnetization reported by Hilscher and Rais (3) showed a compensation point at 105 K. These authors predicted that at this temperature a noncollinear arrangement of the rare earth with iron moments may occur, by applying a strong magnetic field (73.0 Tesla). Our results of lack of saturation of strain at 77 K confirm their conclusion that the compound below 105 K becomes highly anisotropic, in which the anisotropy constants increase drastically.

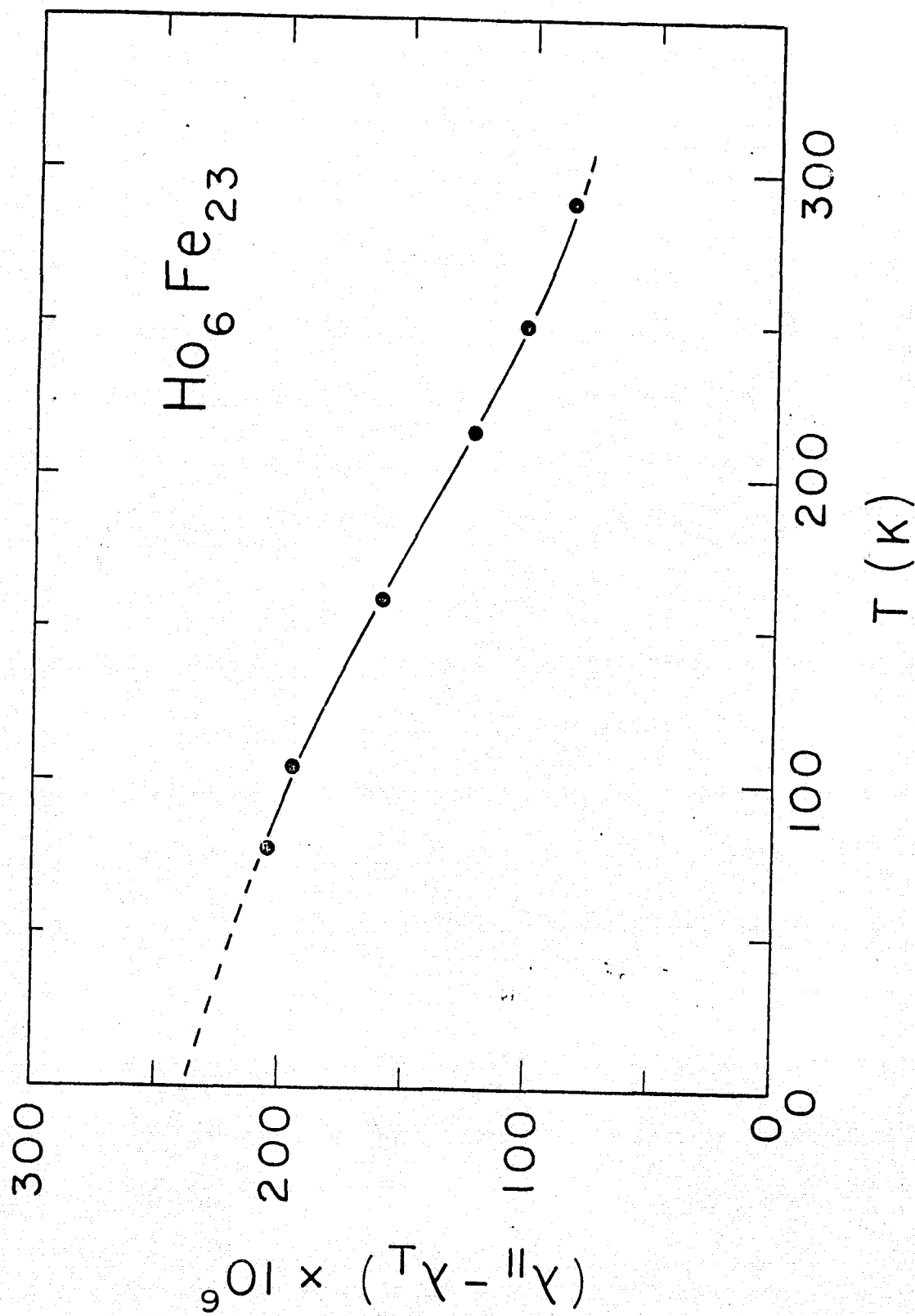


Fig. 7 Temperature dependence of $\chi_{\parallel} - \chi_{\perp} (= \chi_T)$ at 2.1 Tesla for $\text{Ho}_6\text{Fe}_{23}$.

For all the compounds studied the form of λ_t -H curves suggest that magnetostriction constants λ_{100} and λ_{111} for each compound are of the same sign.

The temperature dependence of magnetostriction of $\text{Er}_6\text{Fe}_{23}$ was analyzed and found to follow the single-ion magnetoelectric theory, as treated by Callen and Callen (9):

$$\lambda_t(J) = \lambda_t(0) I_{5/2}[\mathcal{L}^{-1}(m_R)]$$

where $I_{5/2}$ is the reduced hyperbolic Bessel function, \mathcal{L}^{-1} is the inverse Langevin function and m_R , reduced sublattice magnetization of the rare earth ions. Values of sublattice magnetization of Er as a function of temperature were taken from the recent magnetization work of Hilscher and Rais (3). Using $\lambda_t(0) \approx -400 \times 10^{-6}$, the temperature dependence is deduced from the above equation and is shown in Fig. 8. Excellent agreement of the results with the single-ion model is evident. This indicates that the source of the magnetostrictive effects in $\text{Er}_6\text{Fe}_{23}$ is mainly the strain-dependent anisotropy of the Er sublattice.

Assuming that the observed magnetostriction originates primarily with the interaction of the rare earth ions with the crystalline electric field, we can make use of the theory of Tsuya et al. (10) to estimate the saturation magnetostriction of the several R_6Fe_{23} compounds at 0 K, based upon the extrapolated value of λ_t at 0 K (-400×10^{-6}) for $\text{Er}_6\text{Fe}_{23}$; $\lambda_t(0) = C \alpha_J \langle r_f^2 \rangle \langle O_2^0(J) \rangle_{J_2}$ where α_J is the Steven's coefficient (11), $\langle r_f^2 \rangle$ is the mean square of the 4f orbital radius and $\langle O_2^0 \rangle$ is the expectation value associated with crystal field operator O_2^0 . Using the approximation form of the latter, $\langle O_2^0 \rangle_{J=0_2} \approx 2J(J-1/2)$, then the total strain $\lambda_t^{(0)} = C \alpha_J \langle r_f^2 \rangle J (2J-1)$. The resulted calculated using the above method are: $+412 \times 10^{-6}$, $+1040 \times 10^{-6}$ and

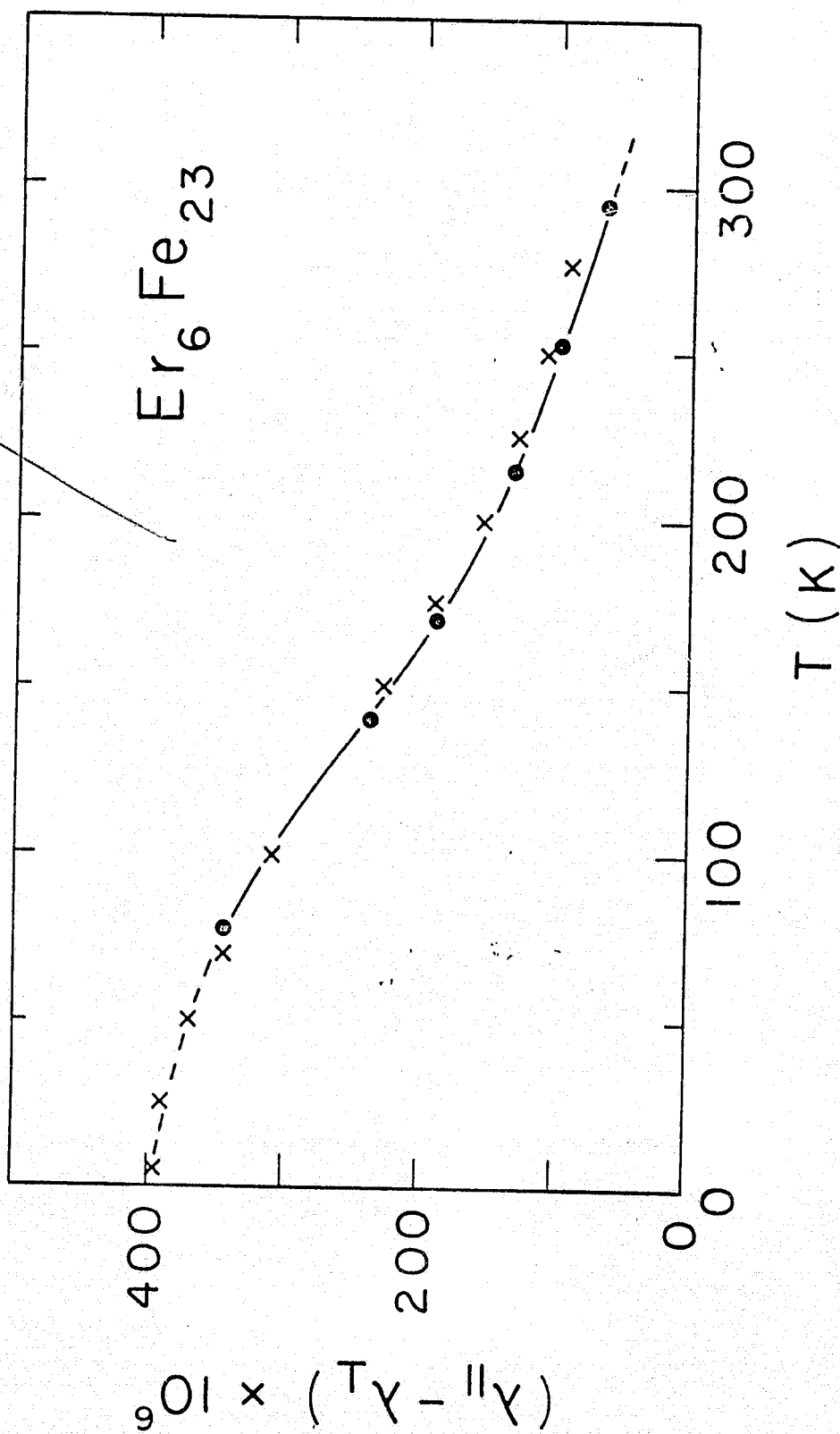


Fig. 8 Temperature dependence of $\lambda_{11} - \lambda_{12} (= \lambda_1)$ for Er_6Fe_{23} . Measured saturation values (●) and values calculated using single-ion theory (x). The solid curve is the best fit through the experimental points. The broken curve is the extrapolated values to 0 K.

$+1080 \times 10^{-3}$ for $\text{Ho}_6\text{Fe}_{23}$, $\text{Dy}_6\text{Fe}_{23}$ and $\text{Tb}_6\text{Fe}_{23}$, respectively. These were compared with the values deduced experimentally. In all cases the signs of $\lambda_L(0)$ deduced from the measurements are in agreement with those predicted by the theory for the corresponding R ions. The magnitudes do not agree exactly.

REFERENCES

- (1) W. E. Wallace, Rare Earth Intermetallics, Academic Press Inc., 1973, Chap. 11. See also K. H. J. Buschow, Rep. Progr. Phys. 40, 1179 (1977).
- (2) O. S. Zarechnyuk and P. I. Kripyakevich, Dopov. Akad. Nauk. Ukr. R. S. R., 1593 (1964).
- (3) G. Hilscher and H. Rais, J. Phys. F. 8-3, 511 (1978).
- (4) A. S. Van der Goot and K. H. J. Buschow, J. Less-Common Metals 21, 151 (1970).
- (5) R. L. Salmans, Tech. Rep. for Wright-Patterson Air Force Base, AFML-TR-68-159 (1968).
- (6) A. E. Clark, AIP Conf. Proc. 18, 1015 (1974).
- (7) E. W. Lee and F. Pourarian, phys. stat. sol.(a) 34, 383 (1976).
- (8) A. E. Clark, R. Abbundi, H. T. Savage and O. D. McMasters, physica 86-88B, 73 (1977).
- (9) E. R. Callen and H. B. Callen, Phys. Rev. 129, 578 (1963).
- (10) N. Tsuya, A. E. Clark and R. M. Bozorth, Proc. Int. Conf. Magn., Nottingham, 250 (1964).
- (11) K. W. N. Stevens, Proc. Phys. Soc.(London) 65, 209 (1952).

Part 2 - Band Structure Calculations

Task 2a

In regard to Task 2a, calculations on selected RCo_5 systems, the work was begun in late 1976 in the immediate aftermath of submitting the proposal to NASA. Calculations were completed on three systems and were published in a paper entitled "Spin-Polarized Energy-Band Structure of YCo_5 , SmCo_5 and GdCo_5 " by S. K. Malik, F. J. Arlinghaus and W. E. Wallace in Physical Review B16, 1242 (1977). Details of those calculations are contained in the published paper. The following is a brief account of the essential findings in this paper.

Band Structure of RCo_5 Compounds

Over the past few years a new class of magnetic materials has come into prominence - intermetallic compounds of the general formula RCo_5 , where R is a rare-earth metal or yttrium. These materials are ferromagnetic, with high Curie temperatures and remarkably large magnetocrystalline anisotropy. They have great technical importance in the fabrication of permanent magnets. Magnets made from SmCo_5 have high coercivity and therefore have very considerable potential for use in the fabrication of electric motors.

In order to understand the electronic and magnetic behaviour of RCo_5 compounds we have calculated, by spin polarized augmented plane wave (APW) technique, the spin-up and spin-down electronic energy bands, the density of states and the magnetic moments of three representatives of the RCo_5 series - YCo_5 , SmCo_5 and GdCo_5 . One important property of these materials is not well understood. The coupling between the electron spins on the cobalt sublattice and those on the rare-earth sublattice is always antiferromagnetic (i.e., antiparallel). This prevents the heavier rare-earth homologs from being useful materials, the net moment being small. The persistence of this coupling scheme,

moreover, cannot be understood in terms of the rather weak Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction; since the RKKY interaction is quite electron-concentration and structure sensitive, variations and exceptions would be expected. Numerous experimental attempts have been made to achieve reversal in coupling between rare-earth and transition-element moments, either by varying electron concentration or by structure changes, but none have been successful. It was hoped that band structure calculations would shed some light on this behaviour.

The band structure results obtained for the three compounds are very similar. The following comments apply to all. The width of the cobalt 3d band complex is ~ 4 eV in each case, for both spin up and spin down. The spin-up and spin-down density-of-states curves are very similar in shape; the results might be approximated by a rigid shift or "exchange splitting" of about 1.6 eV. This 3d-band complex lies in the middle of a typical parabolic s-p band. No other obvious feature can be identified; in particular, no rare-earth band stand out separately. The rare-earth contribution is found hybridized into the cobalt bands, and because there are 45 cobalt electrons to only three rare-earth electrons, the rare earth dominates nowhere. Examination of the separate contributions to the charge density shows a rare-earth contribution almost everywhere, however, and this is important in the aggregate. In all three cases the energy-band curves reveal a completely filled majority-spin 3d subband. The Fermi energy falls in a region of very-low down-spin density of states, though also at a peak in the minority-spin density.

The calculated spin magnetic moments are $7.31\mu_B$ for YCo_5 , $6.49\mu_B$ for GdCo_5 . To compare these with experimental values we must add contributions for orbital moment and for localized 4f moment. The orbital moment has been measured to be $1.746\mu_B$ in YCo_5 by polarized neutron

scattering measurements. Assuming the same value for the other two compounds we get for the total moment values of $9.06\mu_B$ for YCo_5 , $8.24\mu_B$ for SmCo_5 and GdCo_5 . The localized 4f moments are $7\mu_B$ for Gd, typically $0.4\mu_B$ for Sm and no moment for Y. The Gd moment couples antiparallel to the Co moment while the Sm moment couples parallel to the Co moment. Thus, taking into account the 4f moment, we obtain $1.24\mu_B$ as the total moment of GdCo_5 , $8.64\mu_B$ that of SmCo_5 , while the magnetic moment of YCo_5 remains $9.06\mu_B$. These numbers compare well with the experimental values of 8.1 for YCo_5 (neutron diffraction measurements on single crystal YCo_5 yield 8.7 for the same), 8.9 for SmCo_5 and 1.2 for GdCo_5 . We see, therefore, that the spin-polarized APW technique is capable of giving reliable answers for magnetic moments, even in such a complex structure as this.

A more difficult question is whether trends in the band structure are predictable as a function of the rare-earth component involved. In the present case, we have seen that the three band structures are essentially the same. It is hard to be sure that the small differences observed are not random, but an apparent trend is discernible. We see, further, that the principal feature of all three compounds is the 4-eV wide 3d-band complex, that in this respect all three are just cobalt metal. The rare-earth constituent serves principally to present the cobalt in a different crystal structure, giving rise to the large magnetocrystalline anisotropy which makes these materials so interesting in permanent-magnet applications. This provides a natural explanation for the fact that YCo_5 is quite similar to the other RCo_5 's, while yttrium has no 4f electrons; these are not important. The density of states curves in these compounds resemble very much the corresponding curve for pure Co metal - in terms of the location of peaks in the density of states and the location of Fermi energy. Lemaire et al.

[IEEE Trans. Mag., MAG-6, 153 (1970)] first suggested a 3d-band model, but assumed that the three extra electrons from the rare-earth constituent would fill up holes in the rigid minority-spin subband. This would reduce the moment to about $1.1\mu_B$ per cobalt atom, or $5.5\mu_B$ for any RCo_5 , too small a value. The present calculations show that only about one electron per rare-earth atom is transferred to cobalt in each case. The slight differences among the three compounds arise from slight variations in the amount of charge transfer, the exchange splitting, and the hybridization of rare-earth-orbitals with cobalt. The most striking difference occurs between YCo_5 , for which there is a moment of $\sim 0.3\mu_B$ induced on the yttrium site, and SmCo_5 and GdCo_5 , for which the induced moment on the rare-earth site is $\sim 0.1\mu_B$, which is probably zero within the limits of accuracy of the calculation.

Finally, it has been suggested that the antiparallel coupling between rare-earth and cobalt sublattices arises from a RKKY-type mechanism, involving s-d and s-f exchange interactions. In this case, compounds with parallel coupling might be prepared by varying composition or conduction, since the sign of the RKKY interaction is sensitive to electronic concentration. This could lead to much larger magnetic moments. The present calculation casts a pall over such projections, however, by giving evidence of strong d-d coupling (rare earth 4d or 5d with cobalt 3d). This is a much stronger coupling, and implies that the antiparallel spin coupling likely cannot be reversed.

In summary, these calculations provide considerable understanding of the RCo_5 -type compounds. They show the origin of the moment, give good estimates of its magnitude, its variation, and the reasons for those variations. They show the important role of partial charge transfer (band-filling effects) and of d-d electronic coupling.

Task 2b

Calculations are complete for the RNi_5 systems $LaNi_5$ and $GdNi_5$, but these have not yet been submitted for publication. A brief account of the essential findings emerging from these calculations, carried out by Dr. S. K. Malik, is presented in this section.

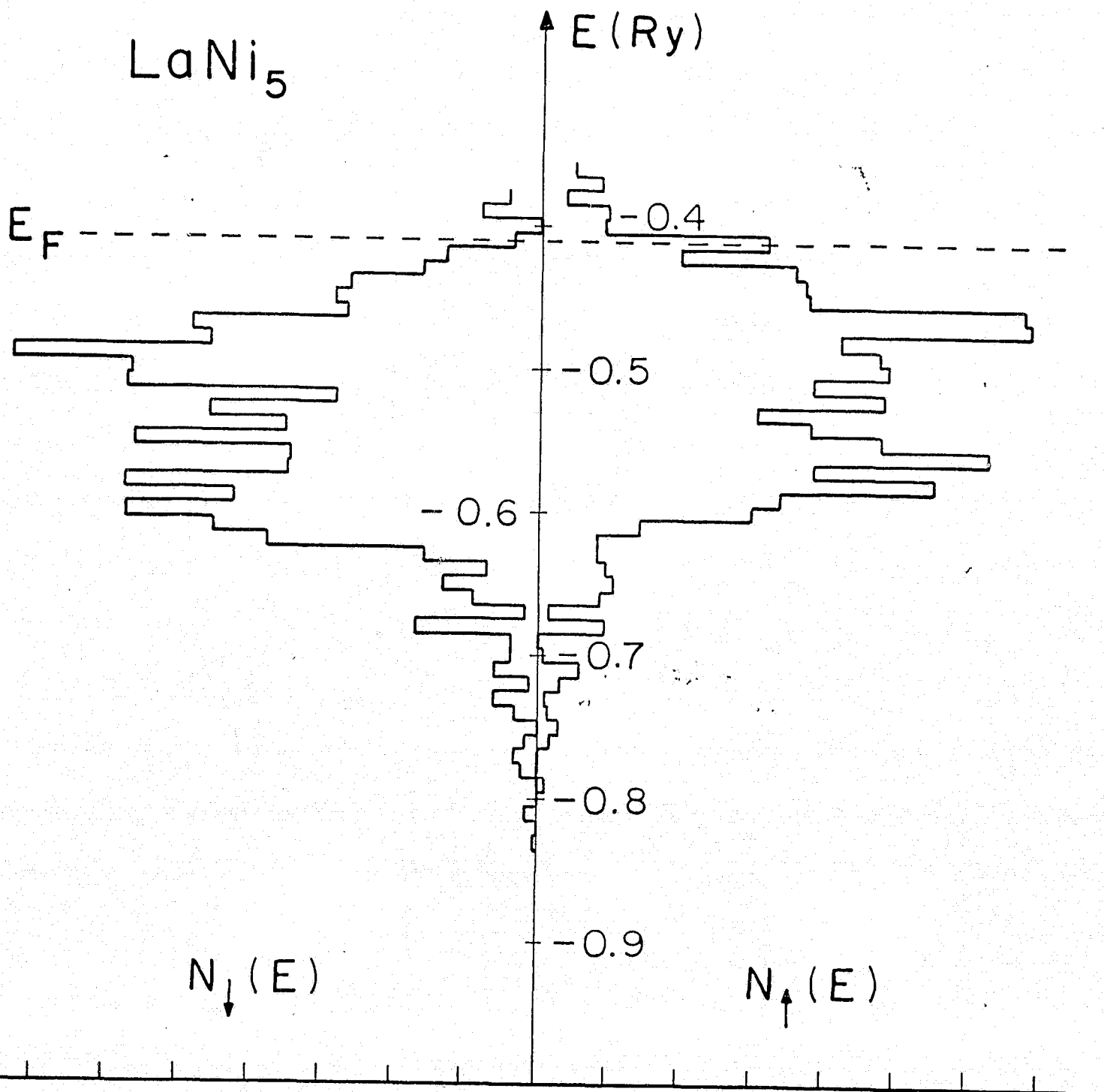
Metal-hydrogen systems have been of interest since the observation about 50 years ago that the element palladium absorbs significant quantities of hydrogen. Interest in this field was further intensified by the discovery that $LaNi_5$ and several other rare earth intermetallics absorb and desorb large amount of hydrogen at ambient temperatures and pressures. These materials are gaining importance because of the hydrogen storage applications - hydrogen being projected as one of the future energy sources. The volumetric capacity of many rare earth intermetallics for hydrogen considerably exceeds that of liquid or solid hydrogen. This property combined with the ease with which hydrogen can be absorbed and desorbed makes them very attractive materials for storage of hydrogen and its subsequent use in fixed plants or vehicular applications.

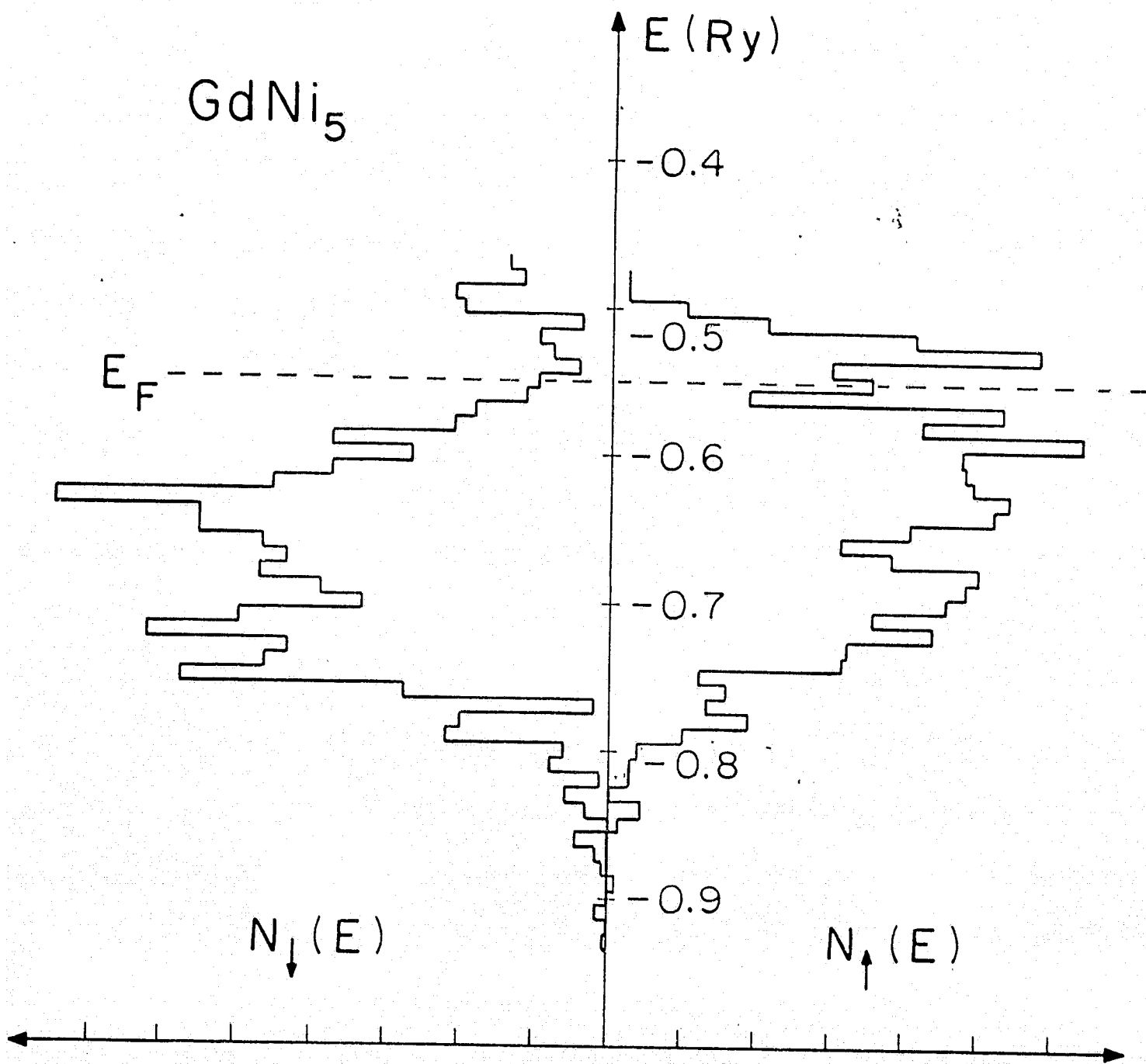
In order to understand the electronic properties and the hydrogen storage characteristics of these rare earth intermetallics, it was decided to carry out electronic band structure calculations on some of these compounds. The compounds $LaNi_5$ and $GdNi_5$ were chosen for this purpose. These compounds are isostructural with the RCO_5 compounds discussed above. This helped to retain the same structural dependent part of computer programs. Further, $LaNi_5$ is one of the best materials to date for hydrogen absorption studies. Another property which is often observed in a series of isostructural compounds is that the capacity to absorb hydrogen decreases as one goes from light to heavy rare earths, e.g., $LaNi_5$ forms $LaNi_5H_6$ while $GdNi_5$ absorbs very little hydrogen. From the viewpoint of magnetic properties pure Ni is a ferromagnet with a magnetic moment of $0.6\mu_B$ per Ni. However, when alloyed with rare earths to form RNi_2 or RNi_5 compounds, Ni loses practically all of the magnetic moment.

Band structure calculations on LaNi_5 and GdNi_5 were carried out using the spin polarized self-consistent APW technique. The results for the two compounds are very similar. The 3d band complex of Ni is about 3.5 eV wide in each case for both spin-up and spin-down electrons. The spin-up and spin-down electronic density of states curves are shown in the diagrams for LaNi_5 and GdNi_5 . For each compound the density of of ^{states} curves for the two spin directions are very similar and may be approximated by a rigid shift or exchange splitting of 0.27 eV for LaNi_5 and 0.4 eV for GdNi_5 . The majority-spin 3d subband is completely filled and the Fermi energy falls in a region of low density of states though in a comparatively larger density of states in the minority-spin 3d subband.

The calculated magnetic moments are $0.14\mu_B$ per Ni in LaNi_5 and $0.18\mu_B$ per Ni in GdNi_5 . These are considerably reduced from the value of $0.6\mu_B$ per Ni for the pure element. Experimentally, the magnetic moment in LaNi_5 is almost zero and is estimated to be $0.05\mu_B$ per Ni in GdNi_5 . Thus the present band structure calculations predict the quenching of magnetic moment in going from elemental Ni to LaNi_5 or GdNi_5 although the extent of quenching as experimentally observed is not predicted. This may be because of the fact that while using the Slater exchange potential of the $x\alpha$ type, we have assumed $\alpha = 1$. This may tend to overestimate the exchange and result in a small net moment on Ni. Probably the best choice for α for these compounds lies between $\alpha = 2/3$ and $\alpha = 1$.

Unfortunately, the band structures of the two compounds are so similar that they do not throw any light on the observation that LaNi_5 absorbs more hydrogen than GdNi_5 . It appears that electronic band structure calculations on these intermetallic-hydrides are required to understand the hydrogen absorption characteristics. The hydrogen wave functions admix with the metal wave functions of the corresponding symmetry, and this causes some levels, which are originally above the Fermi level, to be pulled much below the Fermi level and be available for occupation by metal/hydrogen electrons. Further hydrogen-hydrogen interaction also introduces additional states. Because of the lanthanide

LaNi₅



contraction the wave functions of Gd are likely to be more localized than those of La in RNi_5 series. This may be responsible for greater overlap of R, Ni and H wave functions in $LaNi_5H_6$ than in $GdNi_5H_x$ and be responsible for larger hydrogen absorption by $LaNi_5$. It is desirable to calculate the band structure of the compounds with and without hydrogen and carry out a comparative study of the two (as done by Switendick for some simple metal hydrides) to obtain further information about hydrogen absorption characteristics.

IV. INCOMPLETED PORTIONS OF PROGRAM

A. Magnetostriction Component

The two ultimate objectives of this aspect of the program were (1) - task 1d: to predict materials with large magnetostrictive coefficients and (2) - task 1e: to develop the formalism for optimizing magnetostrictive materials with regard to the various materials' parameters. Task 1c is an essential component of Tasks 1d and 1e.

It is well to review the essential physics underlying magnetostriction of rare earth systems. As indicated above, magnetostrictive effects originate with the rare earth sublattice. The rare earth contribution is a crystal field effect. The crystal distorts to lower the crystal field energy of the system. Distortion occurs against the elastic deformation, raising the energy of the system. A compromise is struck between these two effects and the equilibrium condition is one in which the overall energy is minimized. Consequently, to treat λ in terms of First Principles information in regard to elastic constants is needed. This was to be involved in Task 1c.

Present status of Task 1c: Equipment for obtaining elastic constants by the velocity of sound method has been constructed and calibrated. Preliminary measurements have been made on $\text{Ho}_6\text{Fe}_{23}$ and $\text{Er}_6\text{Fe}_{23}$. Some difficulties were experienced in sample preparation. It is necessary to have a sample of sufficient purity (freedom from extraneous phases) and size. In regard to the latter, fracture of the prepared ingot frequently occurred during cooling. Only the $\text{Ho}_6\text{Fe}_{23}$ and $\text{Er}_6\text{Fe}_{23}$ have been successfully prepared to date.

V. PERSONNEL INVOLVED IN THE PROGRAM

- W. E. Wallace, Principal Investigator
- S. G. Sankar, Co-Principal Investigator (currently at Allied Chemical Corp.)
- S. K. Malik, Ph.D., Research Assistant Professor (Band Structure)
- F. Pourarian, Ph.D., Visiting Assistant Professor (Magnetostriction)
- R. Obermyer, Ph.D., Research Associate, Part-time (Magnetostriction)
- A. Moldovan, Ph.D., Research Associate, Part-time (Band Structure)