A ^{121}Sb Mössbauer Investigation of the Rare Earth Antimonides

P. E. HOLBOURN[1,2] AND F. W. D. WOODHAMS

Sira Institute, Ltd., South Hill, Chislehurst, Kent, England

^{121}Sb Mössbauer spectra have been obtained for the series RSb (R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Yb) at 78 K and for a selection of the compounds at 5.5 K. At 78 K all the spectra show a single line. The isomer shifts are close to that of InSb and show a linear increase with increasing atomic number of the rare earth ion. Many of the rare earth antimonides exhibit a variety of magnetic and structural phase transitions at a sufficiently low temperature. Spectra obtained at 5.5 K are interpreted in terms of these phase transitions.

Introduction

In recent years a considerable research effort has been devoted to studying rare-earth compounds, particularly with a view to understanding their magnetic behavior. A detailed investigation of the members of the rare earth antimonide series is of interest as they crystallize in the simple NaCl-type structure, and so are amenable to theoretical analyses. At a sufficiently low temperature many of these compounds are antiferromagnetic (*1*), and some exhibit, in addition, a structural phase transition (*2, 3*). The magnetic properties depend strongly on parameters such as the number of 4*f* electrons, and the relative strength of the exchange and crystal field interactions, which vary systematically over large ranges within this series.

An extensive theoretical discussion of some of the effects resulting from the interplay between an octahedral crystal field and exchange fields acting on rare-earth ions has been given by Trammell (*4*). It was shown that for an odd number of 4*f* electrons the lowest level is a Kramer's doublet Γ_6, Γ_7 or a quadruply degenerate Γ_8 level, and there will be a magnetically ordered ground state. If the 4*f* shell contains an even number of electrons, the lowest lying crystal field eigenstate will always be a nonmagnetic Γ_1, Γ_2, or Γ_3 level. For such cases no magnetic order can occur unless the exchange field is of sufficient magnitude to mix the higher magnetic levels into the nonmagnetic ground state. This does not happen in a continuous manner; Trammell (*4*) predicted the existence of a threshold value for the ratio of exchange to crystal field interaction, below which magnetic order cannot occur even at zero temperature. Chen *et al.* (*5*) have identified the rare earth antimonides as a class of compounds which display appreciable biquadratic as well as bilinear exchange interactions. They regard such interactions as originating mainly from

0022-4596/81/110186-09$02.00/0

186

indirect quadrupole–quadrupole coupling via the conduction electrons and suggest also that there is a contribution from virtual phonon exchange via the quadrupole–lattice coupling. Such systems may undergo successive but distinct quadrupole and dipole phase transitions, with the structural distortion in the ordered phase then following as a result of the quadrupole–strain coupling. In a recent X-ray study of the lattice distortions of the rare earth actinides, it was noted by Levy (2) that the temperatures at which the distortions occur are significantly higher than the attendant Néel points determined from measurements of the magnetic susceptibility.

It is the purpose of this paper to present the results obtained from a comprehensive Mössbauer investigation of the magnetic and structural behavior of the rare earth antimonides at low temperatures. Mössbauer spectroscopy using the ^{121}Sb nuclide permits the direct measurement of the hyperfine fields at the Sb sites. Deductions may then be made concerning the magnetic and structural phase transitions. Magnetic order occurs as a result of indirect coupling of the localized moments via the conduction electrons. The transferred magnetic field measured at the sites of the nonmagnetic Sb ions then reflect the spin polarization of the conduction electrons at the nuclei via the Fermi contact interaction. The three types of antiferromagnetic order commonly encountered in NaCl-type structures are shown in Fig. 1; oppositely directed moments are depicted by open and closed circles. If the magnetic order is of type 2, each Sb ion is surrounded by three parallel and three antiparallel nearest neighbor magnetic moments, so that the resultant transferred magnetic field at the Sb nucleus is zero. In the type 1 structure each Sb ion is surrounded by four parallel and two antiparallel moments, while the Sb ion in the type 1A structure is surrounded by five parallel and one antiparallel nearest
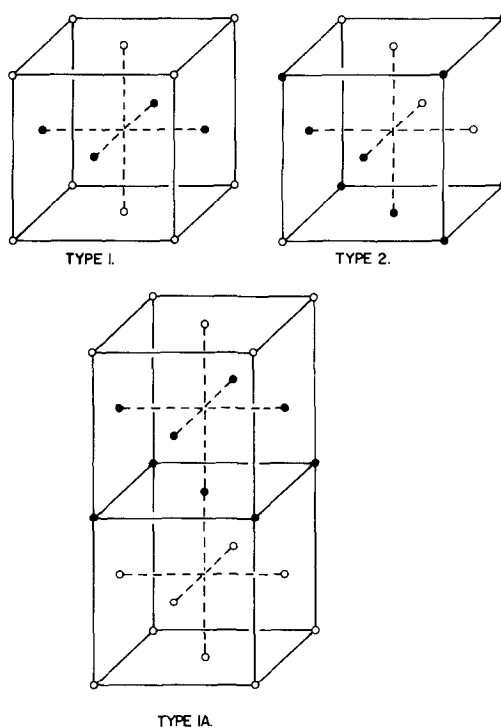

FIG. 1. The three antiferromagnetic structures cited in the text.

neighbor magnetic moments. The transferred field at the Sb nucleus is then nonzero, and in the type 1A structure is approximately double that corresponding to a type 1 structure, assuming the transfer mechanisms are identical. If there is a resultant transferred field, magnetic hyperfine splitting of the Mössbauer resonance line is expected (6). Similarly, if the compound undergoes a structural deformation, an electric field gradient may be expected at the Sb nuclei. This is manifest as an electric quadrupole splitting of the Mössbauer resonance line (7).

Experimental

Stoichiometric quantities of the pure elements were mixed and reacted initially in evacuated, sealed, fused silica ampoules heated slowly ($\frac{1}{3}$ °C/min) to 700°C. The

products were crushed, resealed and annealed, until X-ray powder patterns showed only monophase cubic reflections. Mössbauer absorbers were then fabricated by enclosing a weighed quantity of the powdered sample within a polystyrene disk 28 mm in diameter and 2 mm thick. The absorbers contained either 10 or 15 mg/cm² of Sb.

Transmission spectra were recorded using a constant acceleration, 512-channel microprocessor-controlled spectrometer (8). An absolute calibration of the velocity scale was made with a laser-driven Michelson interferometer as described by Player *et al.* (9). A ^{121m}Sn in $CaSnO_3$ source of nominal strength 1 mCi was used in conjunction with a xenon–methane proportional counter as a γ-ray detector. To enhance the signal to noise ratio, the window of the single-channel analyzer was set on the 7.53-keV escape peak of the 37.15-keV γ-ray. As the count rate in the single-channel analyzer window was only 1100 cps, a period of 3 to 4 days was required for each absorber to accumulate a 512-channel spectrum. The absorbers were mounted on a continuous-flow heat exchanger within an Oxford Instruments liquid helium cryostat which enabled the absorber temperature to be maintained at any required temperature between 5.5 and 300 K.

78-K Spectra

At 78 K the spectra of all the compounds showed a single resonance line with an isomer shift close to that of InSb. The spectrum of GdSb is shown in Fig. 2. The spectra were all computer least-squares fitted to a single Lorentzian shaped line. Mössbauer parameters obtained from these fits are given in Table I, together with their standard deviations quoted with 95% confidence limits.

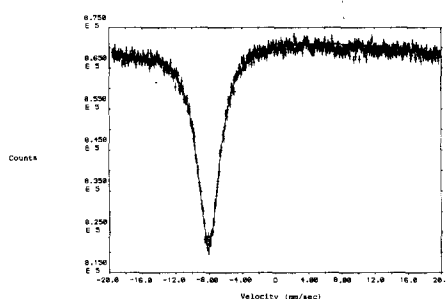Initially, spectra were recorded with both

FIG. 2. Spectrum of GdSb at 78 K fitted to the single-line model.

sample disks of each compound stacked together so that the absorber contained effectively 25 mg/cm² of Sb. However, the linewidths obtained were all between 4.0 and 4.5 mm/sec, indicating a substantial sample thickness broadening effect. Additional spectra taken with the 10-mg/cm² disks showed considerably narrower linewidths of around 3.3 to 3.7 mm/sec, much closer to the values normally associated with single-line Sb absorbers. These linewidths are all slightly greater than that obtained with a sample of InSb having a similar thickness of 10 mg/cm² of Sb, namely, 2.8 mm/sec, indicating a slight inhomogeneity in the samples. There was no evidence of any asymmetric line broadening, such as would occur if there was an electric field gradient at the Sb nuclei. This is not surprising of course as the Sb ions occupy sites of cubic symmetry. No magnetic hyperfine splitting of the resonance line was apparent, since at 78 K, the rare-earth antimonides exhibit paramagnetic behavior (1).

Figure 3 shows clearly that the isomer shift increases linearly with the atomic number of the rare earth ion. Since the nuclear factor $\Delta R/R$ is negative for ^{121}Sb (10) this isomer shift trend corresponds to a decrease in s-electron density at the Sb nucleus with increasing atomic number. One possible explanation is that this trend in isomer shift merely reflects a volume

TABLE I

MÖSSBAUER PARAMETERS

Absorber	IS^a (mm/sec)	LW^b (mm/sec)	$\chi^2\tau^c$	LW^d (mm/sec)	Lattice parameter (Å)
LaSb	0.075(40)	—	1.13	3.93(16)	6.5014(7)
CeSb	0.190(20)	3.15	1.26	3.72(8)	6.4237(0)
PrSb	0.241(14)	2.82	1.25	3.39(8)	6.3822(2)
NdSb	0.301(12)	3.34	1.07	3.71(5)	6.3384(3)
SmSb	0.480(16)	4.02	1.14	4.03(6)	6.2706(10)
GdSb	0.470(16)	2.68	1.15	3.30(6)	6.2194(3)
TbSb	0.463(18)	3.45	1.23	3.62(7)	6.1822(5)
DySb	0.593(14)	—	1.12	3.31(5)	6.1316(3)
HoSb	0.643(16)	3.02	1.14	3.38(6)	6.1307(3)
ErSb	0.675(18)	3.34	1.24	3.68(7)	6.1089(4)
YbSb	0.545(18)	3.32	1.28	3.58(6)	6.0785(3)

[a] Isomer shift with respect to InSb.
[b] Linewidth extrapolated to zero thickness.
[c] Variance ratio (χ^2/number degrees of freedom) for statistically acceptable fit should be less than 1.3.
[d] Linewidth of absorbers containing 10 mg/cm^2 of Sb.
Note. Standard deviations in units of last decimal place, e.g. 0.075(40) stands for 0.075 ± 0.040.

effect. However, it can be seen from Table I that there is an increase in isomer shift with decreasing lattice parameter. As this corresponds to a decrease in s-electron density at the Sb nucleus with decreasing lattice parameter, the isomer shift trend cannot be explained by the compression of the Sb electronic structure by the decrease in cell volume.

This trend in isomer shift is consistent with the covalent bond charge mving towards the rare earth ion as the atomic number increases, with a corresponding reduction in the covalent donation to the 5s orbital of the Sb ion. As the isomer shift is a direct measure of the charge density at the Sb nucleus, some calculations were made in an attempt to correlate the Mössbauer measurements with the charge density and electron population of the Sb ion. Self-consistent calculations were made on LaSb and HoSb within a quasi-relativistic augmented plane-wave scheme developed by Hendry (*11*). Unfortunately the computational methods used proved insufficiently precise to calculate the charge density difference between the Sb nuclei in LaSb and HoSb. From recent free-ion calculations of Ruby (*10*) and the present isomer shift data, a difference of approximately 1 part in 10⁵ is expected for the charge density at the Sb nucleus in these compounds. However, the population analyses of the 5s and 5p or-
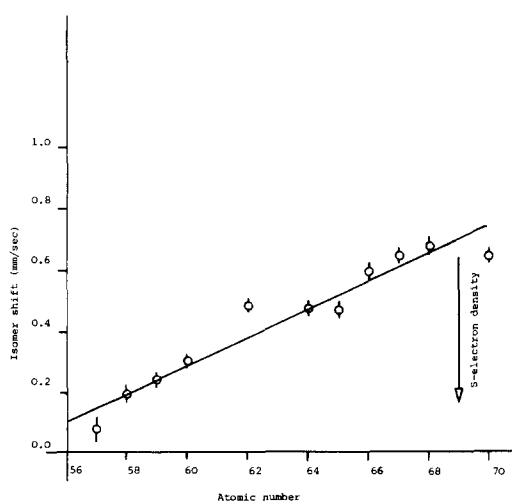

FIG. 3. A plot of isomer shift versus atomic number at 78 K.

bitals of the Sb ions are of interest. The
results, given in Table II, show that the
predominant variation is in the number of
5p electrons with the 5s electron population
remaining relatively constant. Free-ion cal-
culations have shown that the effect of
decreasing the p-electron population is to
decrease the shielding of the s electrons,
and thus to increase the charge density at
the nucleus. However, the charge density is
far more sensitive to changes in the s-
electron population, and the experimentally
determined isomer shifts for LaSb and
HoSb reflect the slight decrease in s-elec-
tron population. These results are in accord
with the isomer shift measurements and
molecular orbital calculations of Pruitt et
al. (12) on the intermetallic Group III anti-
monides.

5.5-K Spectra

Spectra were obtained for the following
compounds at 5.5 K; CeSb, PrSb, NdSb,
GdSb, TbSb, DySb, HoSb, and YbSb. The
spectra were fitted where appropriate to
either a single Lorentizian shaped line or a
combined magnetic and electric quadrupole
model. In general, a $\frac{5}{2}$–$\frac{7}{2}$ $M1$ transition gives
rise to an 18-line spectrum. The natural
linewidth of the ^{121}Sb resonance is such that
hyperfine structure is not usually resolved.
The presence of hyperfine structure is indi-
cated by an asymmetry of the line shape
and, in cases where the hyperfine interac-
tions are large, by structure on the wings of
the resonance line. In these cases informa-

tion regarding the environment of the Sb
site can only be deduced by computer
fitting a selection of models to the spec-
trum, and making judgements from the
quality of fit obtained. This was the tech-
nique used in analyzing the 5.5-K spectra.
A computer program was developed which
calculated the theoretical spectrum from a
given set of hyperfine parameters, and then
varied these parameters in such a way as to
minimize the mean square difference be-
tween the theoretical and the observed
spectrum. To ensure convergence of the
fitting program (13), the following con-
straints were applied: the asymmetry factor
η was chosen to be zero, as the rare earth
antimonides exhibit only slight noncubic
distortions (2); the polar angles (θ) and (ϕ),
describing the orientation of the magnetic
field relative to the principal axis of the
electric field gradient, were fixed at zero.
Finally, to obtain convergence, it was nec-
essary to analyze the spectra with a fixed
linewidth. The linewidths were constrained
to the corresponding values obtained at 78
K, in the absence of magnetic and electric
quadrupole interactions. Although the ac-
tual linewidth is expected to increase on
cooling from 78 to 5.5 K due to an increase
in the recoil-free fraction, this increase will
not markedly affect the results of the com-
puter fits, and the conclusions reached. The
results of these fits are given in Table III.

From the data it is clearly apparent that
the monotonic dependence of the isomer
shift on the rare earth ion is lost at 5.5 K.
This is not surprising. A redistribution of
the electronic charge surrounding the Sb
ion is expected to accompany a second-
order phase transition, as shown by several
of the rare earth antimonides.

CeSb

At 5.5 K the spectrum of CeSb shows
considerable line broadening (Fig. 4), indi-
cating the presence of a transferred
hyperfine field at the Sb nuclei. From the

TABLE II
POPULATION ANALYSIS OF THE Sb ION

	LaSb	HoSb
5s electron population	1.648	1.613
5p electron population	3.077	2.837
Net charge on the Sb ion	0.275	0.550
Isomer shift (mm/sec)	0.075(40)	0.643(16)

TABLE III

MÖSSBAUER PARAMETERS AT 5.5 K

	Single-line model			Combined model				
Absorber	IS (mm/sec)	LW (mm/sec)	χ^2r	IS (mm/sec)	LW^a (mm/sec)	QS^b (mm/sec)	B^c (T)	χ^2r
CeSb	−0.191(40)	5.64(14)	4.81	−0.444	3.72	5.73	6.80	1.46
PrSb	0.048(34)	4.64(14)	5.19	−0.127	3.39	7.56	4.03	3.15
NdSb	0.159(28)	5.43(12)	2.77	0.005	3.71	5.77	5.17	1.26
GdSb	0.437(18)	3.89(6)	1.15					
TbSb	0.400(22)	4.29(8)	2.02	0.490	3.62	5.81	1.77	1.84
DySb	0.508(18)	3.92(6)	2.39	0.453	3.31	5.18	1.87	2.34
HoSb	0.604(18)	3.87(6)	1.07					
YbSb	0.588(20)	4.12(8)	1.95	0.541	3.58	4.56	2.06	1.84
CeSb(14.8 K)	−0.216(50)	5.06(20)	5.62	−0.415	3.72	6.79	4.60	3.82
CeSb(16.4 K)	0.183(27)	3.81(9)	1.41					

[a] Linewidth constrained to value obtained at 78 K.
[b] Ground state quadrupole coupling constant e^2qQ.
[c] Magnetic hyperfine field.

computer fit, a value of 6.8 T was obtained for the transferred magnetic field. This is in good agreement with the results of Shenoy et al. (14), who, from a ^{121}Sb Mössbauer study of CeSb at 4.2 K, reported a transferred field of 6.4 T. As a consequence, the magnetic structure of CeSb must be that of a type 1 or 1A antiferromagnet. It is not possible to differentiate between these alternatives on the basis of the Mössbauer results. However, a recent neutron diffraction study (15) indicated a type 1A structure.
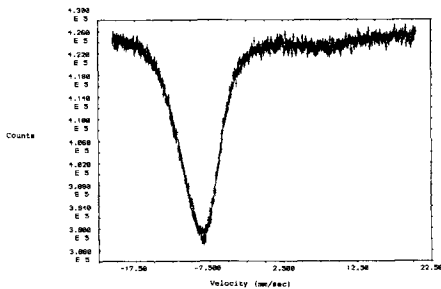

FIG. 4. Spectrum of CeSb at 5.5 K fitted to the combined model.

The nonzero value obtained for the quadrupole splitting demonstrates the departure of the CeSb lattice from cubic symmetry at low temperatures. It has been reported by Levy (2) that the temperatures of the structural phase transitions for the rare earth antimonides are systematically greater than their associated Néel points. This was particularly marked in the case of CeSb, where a tetragonal distortion of the lattice was observed at 19.5 K, followed by a magnetic transition at 16 K. To investigate this phenomena spectra were recorded at 14.8 and 16.4 K. If the antiferromagnetic ordering was to occur at a lower temperature than the structural phase transition, then, in the intermediate temperature region between 16 and 19.5 K, the transferred magnetic field would be zero, and a pure electric quadrupole spectrum would be observed. Values of 4.6 T and 6.79 mm/sec were obtained for the transferred magnetic field and electric quadrupole splitting respectively from the spectrum recorded at 14.8 K. This is consistent with CeSb having undergone both a magnetic and structural

phase transition. However, the spectrum recorded at 16.4 K was adequately fitted to a single-line model. These results suggest that the magnetic and structural phase transitions occur simultaneously.

NdSb

The combined model gave an excellent fit to the spectrum of NdSb. From the magnitude of the transferred magnetic field it was inferred that NdSb was a type 1 or 1A antiferromagnet. This is in accord with the type 1 structure determined by Schobinger-Papamentallos et al. (16) using neutron diffraction techniques. The nonzero value obtained for the electric quadrupole splitting is not unexpected, as it is known from the accurate X-ray measurements of Levy (2) that a tetragonal distortion of the cubic lattic occurs at the Néel point.

PrSb

From measurements on PrSb of the bulk properties, Mullen et al. (3) found no evidence for either a magnetic or structural phase transition down to 1.5 K. However, the spectrum recorded at 5.5 K shows considerable asymmetry and line broadening. A fit to the combined model gave a value of 4.03 T for the transferred magnetic field and 7.56 mm/sec for the electric quadrupole splitting. Thus it was concluded that PrSb undergoes both a magnetic and a structural phase transition, and, as a consequence of the nonzero transferred magnetic field, is a type 1 or 1A antiferromagnet. It is interesting to note that PrSb, in contrast to the type 2 antiferromagnetic structures of the heavy rare earths, shows a type 1 or 1A structure similar to that shown by the light rare earths, CeSb and NdSb. The appearance of magnetic order is surprising, as the crystal field ground state is a Γ_1 singlet. This suggests that the ratio of exchange to crystal field energy exceeds the threshold, predicted by Trammell (4), necessary for magnetic order, even at zero temperatures.

GdSb

The single-line model gave an excellent fit to the spectrum of GdSb at 5.5 K. Although the linewidth of 3.89 mm/sec was slightly greater than that observed at 78 K, namely, 3.3 mm/sec, there was no evidence of either a resultant transferred magnetic field or electric field gradient at the Sb site. Previous susceptibility measurements (1) on GdSb showed the existence of an antiferromagnetic state below a clearly marked Néel temperature of 28 K. In addition, X-ray measurements (2) have shown that this magnetic phase transition is not accompanied by a structural deformation. Thus it may be concluded from the Mössbauer results that GdSb is a type 2 antiferromagnet, and does not exhibit a structural phase transition. This is not unexpected as for GdSb, where Gd^{3+} is an S-state ion, the magnetic charge distribution is spherically symmetric.

TbSb, DySb, and YbSb

At 5.5 K these compounds all exhibit similar asymmetric and slightly broadened spectra. In each case, a fit to the combined model revealed the existence of a small nonzero transferred magnetic field as well as an electric field gradient acting at the Sb site. This may be interpreted as evidence of both a magnetic and structural phase transition. Neutron diffraction measurements (17), (18) have previously demonstrated the existence of a type 2 structure in both TbSb and DySb. The nonzero transferred magnetic field measured at the Sb site must then be attributed to a structural distortion. Confirmation of these observations was provided by Levy (2), who reported a tetragonal and trigonal deformation of the lattice in DySb and TbSb respectively, at the Néel point.

As YbSb has a Γ_6 ground state, the magnetic moment of the Yb^{3+} ion is not quenched by the crystal field. Although

there have been no reports to date of a magnetic phase transition, exchange interactions can give rise to a magnetically ordered state at a sufficiently low temperature. The Mössbauer results show that YbSb exhibits both a magnetic and structural phase transition. Although a neutron diffraction investigation is required to determine the magnetic structure exactly, it is reasonable to conclude that as the transferred field is of the same order as that in DySb and TbSb, that YbSb possesses a type 2 antiferromagnetic structure similar to that exhibited by the other heavy rare earths.

HoSb

A Néel point of 5.5 K has been quoted by Busch et al. (*1*) for HoSb. In addition, a tetragonal deformation of the lattice has been observed to accompany the magnetic phase transition (*2*). Thus an electric field gradient is expected at the Sb site. However, the spectrum recorded at 5.5 K, the lowest temperature obtainable in the cryostat available, was satisfactorily fitted to a single-line model. It was concluded that the Néel point had not been attained.

It was not considered worthwhile recording the spectra of LaSb, SmSb, and ErSb at 5.5 K. LaSb has the electronic structure $4f^{0}$ and so cannot order, while Néel points of 2.1 and 3.5 K have been reported for SmSb and ErSb, respectively.

Conclusions

At 78 K the rare earth antimonides all exhibit single-line spectra. The isomer shifts are all close to that of InSb and show a linear increase with increasing atomic number of the rare earth ion. This is consistent with the covalent donation to the $5s$ orbital of Sb decreasing with atomic number of the rare earth ion; i.e., the covalent bond charge moves towards the rare earth ion as the atomic number increases. Theo-

retical calculations show, however, that although the $5s$ population does decrease slightly with increasing atomic number, the predominant variation is the increase in the $5p$ population of the Sb ion with increasing atomic number of the rare earth ion.

Mössbauer spectra of the rare earth antimonides obtained at 5.5 K reveal a variety of hyperfine interactions. From the measured values of the transferred hyperfine field it was concluded that CeSb and NdSb undergo a structural deformation and exhibit type 1A and 1 antiferromagnetic order respectively, in agreement with recent neutron diffraction measurements. In addition, spectra of CeSb recorded at 14.8 and 16.4 K show a single first-order magnetic phase transition which is accompanied by a structural deformation. The present results show that GdSb is a type 2 antiferromagnet but does not deform; at 5.5 K GdSb retains the NaCl-type structure. In contrast, the spectra recorded for TbSb and Dy Sb were found to be consistent with a type 2 antiferromagnetic structure which has undergone a structural deformation. From an analysis of the spectra of PrSb and YbSb it was found that they both exhibit a magnetic and a structural phase transition. It was concluded, tentatively, from the measured values of the hyperfine fields that PrSb shows type 1 or 1A antiferromagnetism while YbSb is a type 2 antiferromagnet. A detailed neutron diffraction study is necessary to elucidate the magnetic structure exactly.

Acknowledgment

References

1. G. BUSCH, O. MARINECK, A. MENTH, AND O. VOGT, *Phys. Lett.* **14**, 262 (1965).