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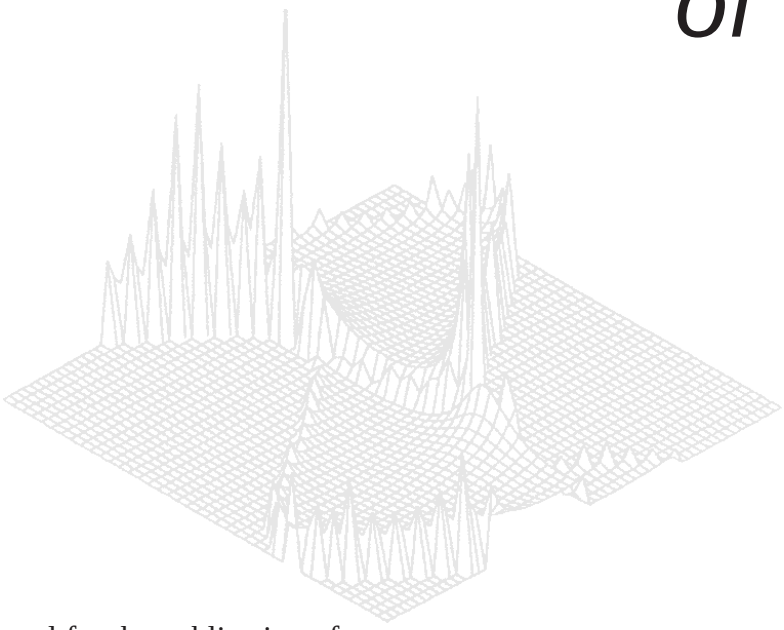

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Hyperfine Field and Induced Moment of ^{181}Ta in the Rare Earth–Iron Laves Compounds*

B. A. Komissarova,[A] *G. K. Ryasny,*[A] *L. G. Shpinkova,*[A] *A. A. Sorokin,*[A] *A. V. Tsvyashchenko,*[B] *L. N. Fomicheva*[B] *and A. S. Denisova*[C]

[A] Institute of Nuclear Physics, Moscow State University, 119899, Moscow, Russia.
[B] Institute of High Pressure Physics, Russian Academy of Sciences, 142092, Troitsk, Moscow, Russia.
[C] Institute of Crystallography, Russian Academy of Sciences, 117333, Leninskii pr. 59, Moscow, Russia.

Abstract

The hyperfine magnetic fields and their temperature dependence for ^{181}Ta in $ErFe_2$ and $TmFe_2$ have been measured by the TDPAC method. Respectively, the following values were obtained at $T \approx 80$ K: $16 \cdot 3(2)$ T and $17 \cdot 6(2)$ T. These data complete those for other RFe_2 Laves phases (except $CeFe_2$) obtained earlier and are discussed in common in the framework of the model predicting the induction of the localised 5d moment at Ta ions due to 5d–3d band hybridisation enhanced by the 4f–5d interaction.

1. Introduction

The problem of the interaction of well localised magnetic moments of rare earth ions (R) and the itinerant transition metal (T) magnetism in the RT intermetallic compounds is now being extensively studied, both experimentally and theoretically. Of these compounds, the Laves phases RFe_2 are the most popular objects due to their comparatively simple crystal structure (cubic C15), and well established macroscopic magnetic properties (Wallace 1973). It is also important that the band structure of similar compounds AFe_2 (where A stands for the 4d and 5d transition metals: Y, Zr, Lu, Hf, etc.) is now sufficiently well understood (for a review see Yamada 1988). In particular, it was shown that the 3d–4(5)d band hybridisation induced a localised moment at A sites of about $0 \cdot 5\ \mu_B$, antiparallel to the Fe 3d moments.

There exists also ample experimental evidence confirming this important conclusion for the host A elements: Y in YFe_2 (Armitage *et al.* 1989; Ritter 1989), Zr in $ZrFe_2$ (Dumelow and Riedi 1987; Warren *et al.* 1992), Hf in $HfFe_2$ and Lu in $LuFe_2$ (Baudelet *et al.* 1993), and an impurity: Nb in $ZrFe_2$ (Dumelow and Riedi 1987). As early as 1980 we proposed the existence of such a localised moment at the impurity Ta ions in the pseudo-binary Laves compound $(Zr_{1-x}Hf_x)Fe_2$ on the basis of studying the hyperfine magnetic field, and its temperature dependence,

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on ^{181}Ta nuclei (daughter of ^{181}Hf) using the time-differential perturbed angular correlation method (TDPAC) (Komissarova *et al.* 1980; for more details see Akselrod *et al.* 1983).

Due to the existence of the induced localised moment μ_A at A sites the hyperfine field at the nuclei of A ions can be represented as a sum of two main contributions:

$$B_{hf}(A) = B_{CP} + B_{CEP}\,,$$

where B_{CP} is due to core polarisation from the moment μ_A, and B_{CEP} is the contribution from the conduction electron polarisation. Thus, the contribution B_{CP}, which is of the opposite sign with respect to B_{CEP} (and smaller in absolute value), can be considered as a measure of μ_A though, as stated by Coehoorn (1989), due to its broader spatial distribution than those of Fe moments 'a constant conversion factor of the hyperfine field to the local moment is not a good approximation'.

Our further studies of hyperfine interactions of ^{181}Ta in AFe_2 (A = Y and Lu) and $Zr(Fe_{1-x}T_x)_2$ (T = Mn or Co) have shown that B_{hf}(Ta), and namely B_{CP}, is very sensitive to certain features of the hybridised d-band of these systems, presumably due to extra valence 5d electrons at the Ta site (Sorokin *et al.* 1994).

Our earlier experiment on the hyperfine interaction of ^{181}Ta in $LuFe_2$ gave the value of the hyperfine field (Kochetov *et al.* 1990)

$$B_{hf}(\mathrm{Ta} : LuFe_2) = -20{\cdot}5\ \mathrm{T}\,,$$

which can be compared with that for Lu (Kasamatsu *et al.* 1995):

$$B_{hf}(\mathrm{Lu} : LuFe_2) = -47{\cdot}8\ \mathrm{T}\,.$$

The difference of about 27 T should be attributed to an increased value of B_{CP} for Ta due to higher 5d electron density at its site (the atomic valence electron configuration of Ta is $5d^36s^2$ compared with $5d^16s^2$ for Lu).

According to recent studies, magnetic properties of RT intermetallics are to a large extent determined by the 5d conduction electrons of R ions. The calculations of Brooks *et al.* (1989, 1991), performed for RFe_2 Laves phases with heavy lanthanides (Gd–Yb), show that the interaction of localised 4f moments with itinerant Fe 3d electrons is mediated, mainly, by hybridisation of the Fe 3d band electrons and the 5d electrons of R ions, the latter being polarised due to the local 4f–5d exchange. As a result, a quasi-local 5d spin polarisation is induced at the R sites, antiparallel to the 3d polarisation. These calculations predict a linear proportionality of the 5d, as well of the 3d, polarisation to the 4f spin. It can be proposed that an induced moment of the 4d or 5d substitutional impurity at R sites, such as e.g. Ta, can be used as a probe sensing changes of the hybridised d-band polarisation due to changes of the 4f moment, and that these changes can be detected by observing the hyperfine interaction of the impurity nuclei.

Here we report the results of the TDPAC studies of the magnetic hyperfine interaction of ^{181}Ta in $ErFe_2$ and $TmFe_2$, which complete the series of our experiments in the whole range of the RFe_2 compounds for R from Pr to Yb.

The data for $NdFe_2$ (Sorokin *et al.* 1993), $SmFe_2$ (Ryasny *et al.* 1994), $GdFe_2$ (Sorokin *et al.* 1992), $PrFe_2$, $DyFe_2$ and $YbFe_2$ (Sorokin *et al.* 1997*a*), and $TbFe_2$ and $HoFe_2$ (Sorokin *et al.* 1997*b*) were published earlier.

2. Experimental

The samples were prepared by re-melting of about 500 mg of $HoFe_2$ and $TmFe_2$, synthesised beforehand, with a small amount ($<0{\cdot}5$ wt.%) of $HfFe_2$ in which ^{181}Hf was activated by neutron irradiation in a reactor. We used the same method of melting and quenching at high pressure (8 Gpa) that was used for preparation of $PrFe_2$, $NdFe_2$ and $YbFe_2$ which cannot be synthesised otherwise (Cannon *et al.* 1972). This method, described in more detail by Tsvyashchenko (1984), ensured preparation of the single phase C15 samples with ^{181}Hf activity uniformly distributed over their volume. The ^{57}Fe Mössbauer spectra of our samples reproduced those published for the pure $ErFe_2$ (Bowden *et al.* 1968) and $TmFe_2$ (Bleaney *et al.* 1982) quite well. For the TDPAC measurements the samples were crushed and small shiny pieces from their cores were used as sources.

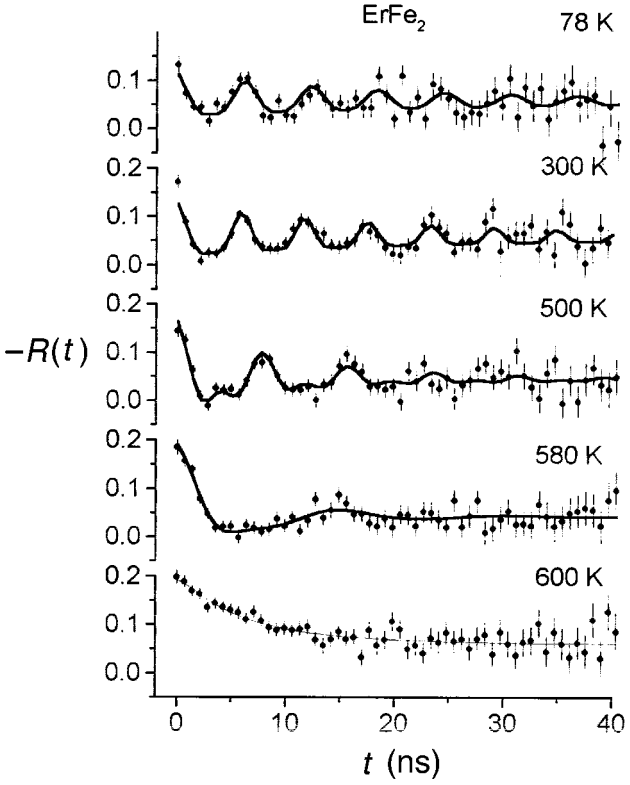

Fig. 1. TDPAC spectra for ^{181}Ta in $ErFe_2$ for different temperatures.

The three-detector scintillation coincidence spectrometer with time resolution $2\tau_0 = 1{\cdot}8$ ns at the energies of the 133–482 keV γ-ray cascade was used in the

measurements which were performed at temperatures from ≈80 K up to 700 K, i.e. well above the Curie points of these compounds, $T_C \approx 580$ K for $ErFe_2$ and ≈600 K for $TmFe_2$.

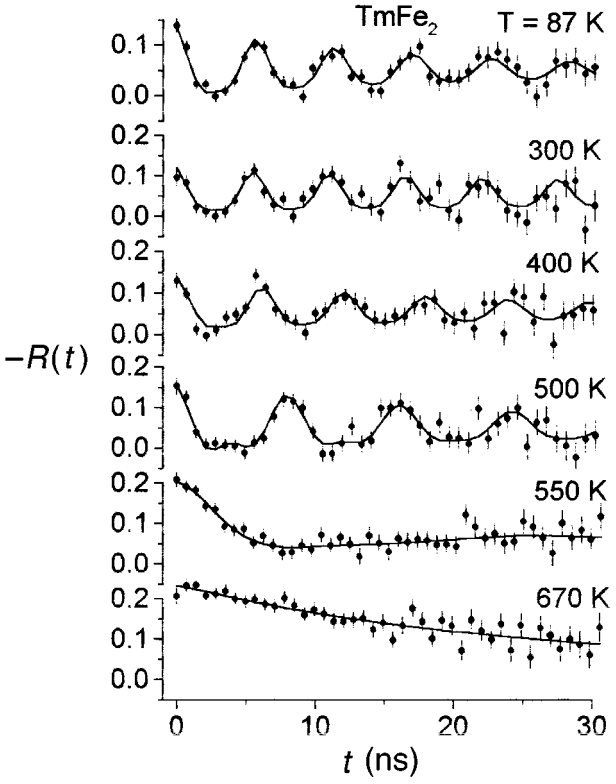

Fig. 2. TDPAC spectra for ^{181}Ta in $TmFe_2$ for different temperatures.

The examples of the TDPAC spectra are shown in Fig. 1 ($ErFe_2$) and Fig. 2 ($TmFe_2$). Below T_C the spectra were fitted assuming the purely magnetic hyperfine interaction in samples with randomly oriented domains. At room temperature the following values of hyperfine fields were obtained:

$$B_{hf}(\mathrm{Ta} : \mathrm{ErFe_2}) = 17 \cdot 3(2)\ \mathrm{T}; \qquad B_{hf}(\mathrm{Ta} : \mathrm{TmFe_2}) = 18 \cdot 2(2)\ \mathrm{T}\,.$$

The relative width of the Larmor frequency distribution due to lattice imperfections was about 3% in both cases. About 80% of ^{181}Ta nuclei (and hence the parent ^{181}Hf) experienced these fields, the other ≈20% occupying some 'unobservable' sites. The lattice imperfections also define a slow monotone damping of the correlation anisotropy above T_C, due to a random electric quadrupole interaction.

The slow damping of the precession pattern at a single Larmor frequency and the absence of quadrupole interaction with a definite frequency allowed us to ascribe the observed hyperfine fields to the substitutional sites of the ^{181}Hf–^{181}Ta probe in the R-sublattice, possessing the cubic point symmetry. In this case we have not performed measurements with magnetised samples for determination

of the $B_{\rm hf}$ sign, but in all other cases where we had done so ($NdFe_2$, $GdFe_2$, $TbFe_2$, $LuFe_2$) it was negative with respect to the Fe 3d moments, i.e. negative with respect to the bulk magnetisation in ferromagnetic $NdFe_2$ and $LuFe_2$, and positive in ferrimagnetic $GdFe_2$ and $TbFe_2$.

The temperature dependence of hyperfine fields in these samples is shown in Fig. 3. It is seen that in both cases the hyperfine fields approach zero near the Curie points quoted above, but do not follow the bulk magnetisation of these ferrimagnetic substances, in which there are compensation points at ≈500 K ($ErFe_2$) and ≈250 K ($TmFe_2$) (Burzo 1971). A noticeable decrease of $B_{\rm hf}$ is seen with decreasing temperature below ≈300 K. This behaviour is characteristic for all RFe_2 phases, and in some cases is much more prominent, e.g. in $NdFe_2$, $SmFe_2$, $GdFe_2$ and $TbFe_2$.

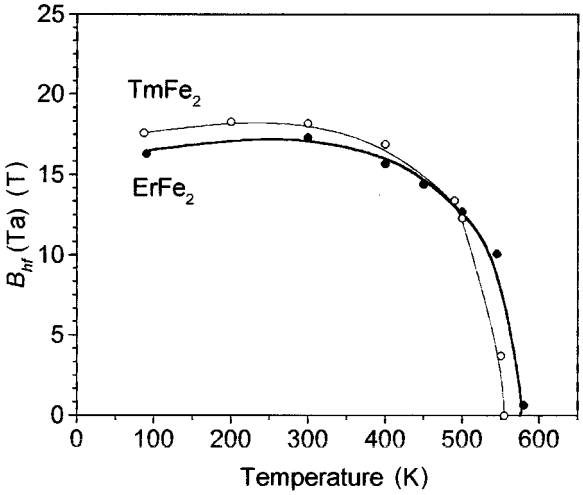

Fig. 3. Temperature dependence of hyperfine fields of $B_{\rm hf}$(Ta) in $ErFe_2$ and $TmFe_2$.

The peculiarities of the temperature dependence of $B_{\rm hf}$(Ta) in the low temperature region are indicative of different temperature dependencies of the two contributions into the hyperfine field at Ta.

3. Discussion

The results of this experiment can be compared with the data for other RFe_2 compounds. In Table 1 the values of $B_{\rm hf}$(Ta) are presented for $T = 300$ K and ≈80 K, when all the contributions are close to saturation, together with some of the main properties of the RFe_2 intermetallics. It is seen that in all cases the $B_{\rm hf}$ are lower than that for $LuFe_2$ in which the 4f shell is closed. The $B_{\rm CEP}$ contribution along the RFe_2 series is believed to be nearly constant (Steiner 1979), at least for heavy lanthanides, and amounts to ≈80 T. It can be assumed that $B_{\rm CEP}$ for the Ta impurity ion is also constant in these phases but somewhat lower due to a different hyperfine coupling constant. Analysis of the data on the hyperfine interactions of Lu in $LuFe_2$ allowed us to estimate a value of $B_{\rm CEP}$ for Lu as being ≈60 T, and to propose that a similar value can be accepted for Ta in RFe_2 phases.

Table 1. Hyperfine magnetic fields at ^{181}Ta in the Laves phases RFe_2 for $T = 300$ K and ≈80 K

The experimental uncertainties in all cases are ≈0·2, except $DyFe_2$ for which they are ≈0·5 T at 300 K and ≈0·9 T at 80 K. The data for the lattice constants and Curie points are compiled on the basis of references cited in the text. The sign of B_{hf}(Ta) in all cases is determined with respect to the bulk magnetisation

R ion	a (Å)	T_C (K)	Magnetic structure	B_{hf}(Ta) (T) 80 K	300 K
Pr	7·47	543	Ferro	6·7	7·6
Nd	7·45	578	Ferro	−5·5	−6·9
Sm	7·42	676	Ferri	7·1	8·4
Gd	7·39	796	Ferri	7·4	9·3
Tb	7·35	697	Ferri	9·8	12·1
Dy	7·32	630	Ferri	14·2	14·6
Ho	7·30	608	Ferri	15·0	16·2
Er	7·28	587	Ferri	16·3	17·3
Tm	7·23	600	Ferri	17·6	18·2
Yb	7·24	560	Ferri	18·0	18·5
Lu	7·22	596	Ferro	20·5	20·5

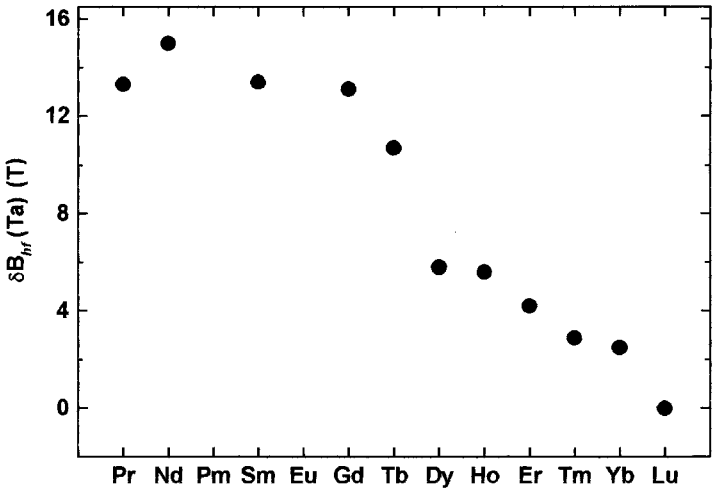

Fig. 4. Difference of $LuFe_2$ and RFe_2 hyperfine fields at ^{181}Ta in the R sequence from Pr to Lu.

In Fig. 4 the difference $\delta B_{hf}(\text{Ta}) = B_{hf}(\text{Ta: } LuFe_2) - B_{hf}(\text{Ta: } RFe_2)$ is shown, and it is seen that it increases monotonically from $LuFe_2$ to $GdFe_2$, and this growth is approximately linear, at least up to $DyFe_2$. This growth correlates with increasing 4f spin, which can be considered a consequence of an increase in the Ta moment due to an enhanced d-band polarisation predicted by the calculations of Brooks *et al.* (1989, 1991) cited above.

In the region of lighter rare-earth ions, from $GdFe_2$ to $PrFe_2$, δB_{hf}(Ta) is practically constant (≈15 T) in spite of different 4f total and spin moments of R ions and different types of magnetic ordering: ferrimagnetic for $GdFe_2$ and

$SmFe_2$ (for the latter this type of ordering was proposed by Dublon *et al.* 1975) and ferromagnetic for $NdFe_2$ and $PrFe_2$ (Meyer *et al.* 1981). Unfortunately, experimental and theoretical data concerning the electron structure for the light group of the RFe_2 compounds are too scarce to be used for an explanation of this observation.

4. Conclusion

The hyperfine magnetic fields at ^{181}Ta nuclei in $ErFe_2$ and $TmFe_2$, and their temperature dependence were measured. The comparison with these data with those for other RFe_2 Laves phases suggests that there exists an additional positive contribution to the hyperfine field in the compounds with rare earths with unfilled 4f shells as compared to that in $LuFe_2$ where the 4f shell of Lu is closed. In the range of R ions from Yb to Dy a linear correlation of this increment with the 4f spin is observed; in the lighter part, from Gd to Pr, this contribution is the largest ($\approx$15 T) and independent of the 4f moment and the type of magnetic ordering.

Acknowledgments

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References

Akselrod, Z. Z., Budzynski, M., Komissarova, B. A., Kryukova, L. N., Reiman, S. I., Ryasny, G. K., and Sorokin, A. A. (1983). *Hyperfine Interact.* **14**, 7.

Armitage, J. G. M., Dumelow, T., Riedi, P. C., and Abell, J. S. (1989). *J. Phys.* C **1**, 3987.

Baudelet, F., Giorgetti, Ch., Pizzini, S., Brouder, Ch., Daryge, E., Fontaine, A., Kapplere, J. P., and Krill, G. (1993). *J. Elect. Spectrosc. Related Phenomena* **62**, 153.

Bleaney, B., Bowden, G. J., Cadogan, J. M., Day, R. K., and Dunlop, J. B. (1982). *J. Phys.* F **12**, 795.

Bowden, G. J., Bunbury, D. St. P., Guimaraes, A. P., and Snyder, R. E. (1968). *J. Phys.* C *(Proc. Phys. Soc.),* ser. 2, **1**, 1376.

Brooks, M. S. S., Eriksson, O., and Johansson, B. (1989). *J. Phys.* C **1**, 5861.

Brooks, M. S. S., Nordstrom, L., and Johanssson, B. (1991). *J. Appl. Phys.* **69**, 5683.

Burzo, E. (1971). *Z. Anges. Phys.* **32**, 127.

Cannon, J. F., Robertson, D. L., and Hall, H. T. (1972). *Mat. Res. Bull.* **7**, 5.

Coehoorn, R. (1989). *Phys. Rev.* B **39**, 13072.

Dublon, G., Dariel, M. P., and Atzmoni, U. (1975). *Phys. Lett.* A **51**, 262.

Dumelow, T., and Riedi, P. C. (1987). *Hyperfine Interact.* **34**, 407.

Kasamatsu, Y., Armitage, J. G., Lord, J. S., Riedi, P. C., and Fort, D. (1995). *J. Mag. Magn. Mater.* **140–4**, 819.

Kochetov, O. I., Sarzinski, J., Tsupko-Sitnikov, V. M., Akselrod, Z. Z., Komissarova, B. A., Krylov, V. I., Kryukova, L. N., Ryasny, G. K., Shpinkova, L. G., and Sorokin, A. A. (1990). *Hyperfine Interact.* **59**, 521.

Komissarova, B. A., Kryukova, L. N., Ryasny, G. K., and Sorokin, A. A. (1980). Fifth Conf. on Hyperfine Interactions, Book of Abstracts, C59–1 (West Berlin).

Meyer, C., Hartmann-Boutron, F., Gros, Y., and Berthier, Y. (1981). *J. Phys. (Paris)* **42**, 605.

Ritter, C. (1989). *J. Phys.* C **1**, 2765.

Ryasny, G. K., Sorokin, A. A., Akselrod, Z. Z., Shirani, E. N., Komissarova, B. A., Kryukova, L. N., and Shpinkova, L. G. (1994). *Solid State Commun.* **92**, 741.

Sorokin, A. A., Ryasny, G. K., Komissarova, B. A., Shpinkova, L. G., Shirani, E. N., Krylov, V. I., Tsvyashchenko, A. V., Fomicheva, L. N., and Panova, T. O. (1992). *Solid State Commun.* **81**, 65.

Sorokin, A. A., Ryasny, G. K., Komissarova, B. A., Shpinkova, L. G., Shirani, E. N., Tsvyashchenko, A. V., and Fomicheva, L. N. (1993). *Solid State Commun.* **88**, 529.
Sorokin, A. A., Komissarova, B. A., Shpinkova, L. G., Ryasny, G. K., and Shirani, E. N. (1994). *Izv. Akad. Nauk, ser. fiz.* **58**, 10.
Sorokin, A. A., Komissarova, B. A., Ryasny, G. K., Shpinkova, L. G., Akselrod, Z. Z., Tsvyashchenko, A. V., Shirani, E. N., and Fomichova, L. N. (1997*a*). *Sov. Phys. JETP* **84**, 599.
Sorokin, A. A., Komissarova, B. A., Ryasny, G. K., Reiman, S. I., Spinkova, L. G., Denisova, A. S., Tsvyashchenko, A. V., Shirani, E. N., and Fomichova, L. N. (1997*b*). *Vestnik Moskovskogo Universiteta, ser. fizika, astronomiya* **5**, 26.
Steiner, W. (1979). *J. Mag. Magn. Mater.* **14**, 47.
Tsvyashchenko, A. V. (1984). *J. Less-Comm. Met.* **9**, L9.
Wallace, W. E. (1973). 'Rare Earth Intermetallics' (Academic: New York).
Warren, P., Forsith, J. B., McIntyre, G. J., and Bernoef, N. (1992). *J. Phys.* C **4**, 5795.
Yamada, H. (1988). *Physica* B+C **149**, 390.

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