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Mössbauer Spectra of Several Ternary Silicides, Germanides, and Antimonides of Transition Metals

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Preliminary Mössbauer results on ternary silicides, germanides, and antimonides of transition metals are presented. They are discussed in terms of the crystallographic data and compared with previous work on similar phosphides.

1. Introduction

Previously, we have studied by Mössbauer spectroscopy the magnetic and electronic behavior of phosphides and arsenides of transition metals (*1*). In order to complete these studies, we investigate here some ternary silicides, germanides, and antimonides with formula *TT*′Si(Ge, Sb) where *T* stands for a large electropositive transition metal (Ti, for instance) while *T*′ stands for a metal in the iron group.

The crystallographic properties of the ternary silicides and germanides were extensively studied by Johnson and Jeitschko [see for instance Refs. (*2*, *3*)].

Many binary or ternary antimonides with formula *TT*′Sb in which *T* and *T*′ are transition metals were investigated by numerous workers with various techniques.

We present here preliminary Mössbauer results on several members of these three series. Table I gives the structures of the studied compounds and the eventual ordering of the metallic atoms on the sites in the structure.

All these structures are characterized by the existence of two or three different sites for the atoms. We denote the sites by I, II, III.

For the Cl_b structure of MgAgAs, the Mg site is I, the Ag site is II, and the As site is III (*4*).

In the Fe_2P hexagonal structure, there are two sites for *T* and *T*′ atoms: one site (I) shows a tetrahedral environment of P, whereas the other one (II) shows a pyramidal environment of P (*5*). The distorted version of this structure observed in TiFeSi offers more possibilities for the metal atoms. Class I is subdivided into two subclasses, whereas class II is subdivided into three subclasses which are differentiated only by the distances between the Fe or Ti and the Si atoms. The population ratio in site I is 2/1 (*6*).

The orthorhombic anti-$PbCl_2$ structure of TiNiSi like Fe_2P has two sites for *T* and *T*′ and Si replaces P (*2*).

In the Ni_2In hexagonal structure, two sites are available for the metallic atoms; one is octahedral (II) and the other trigonal–bipyramidal (I) (*3*).

Except for VCoSb, little is known about the magnetic properties of the compounds

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TABLE I

CRYSTALLOGRAPHIC DATA

Compound	Structure	Site I	Site II	Site III
TiMnSi	Fe_2P (hex)			
TiFeSi	TiFeSi (distor. Fe_2P hex)	Fe (two types popul.: 2/1)	Ti	
TiCoSi	TiNiSi (anti-$PbCl_2$) orthorhomb.	Co	Ti	
TiNiSi	TiNiSi	Ni	Ti	
$MnFe_{0.5}Ni_{0.5}Si$	TiNiSi	Fe[a]		
NbFeSi	TiNiSi	Fe	Nb	
TiFeGe	TiFeSi	Fe	Ti	
MnFeGe	Ni_2In (hex.)	Fe	Mn	
VCoSb	MgAgAs $C1_b$ cubic	Sb	V	Co
VFeSb	MgAgAs	Sb	V	Fe[a]
TiCoSb	MgAgAs	Sb	Ti	Co

[a] Site occupation deduced from this work.

discussed here. VCoSb has a Curie temperature of 75°K and an effective moment of 1.26 μ_B/form (*4*). Its magnetic behavior is similar to that of $ZrZn_2$ but cannot be entirely explained by the theory of band model for itinerant ferromagnetism.

2. Experimental

All the compounds have been prepared by direct combination of the pure elements mixed and sealed in a quartz tube which has been heated at 900°C for several days. Except for TiMnSi and TiFeGe, they have been reground and refired between 900 and 1000°C for another several days. Furthermore, a single-phase NbFeSi sample has been obtained on heating at 1250°C for 1 day. All the compounds have been slowly cooled down to room temperature (at a rate of 40°/hr). When needed for the Mössbauer study, ^{57}Fe has been introduced by one firing at 850°C in vacuum. X-Ray diffraction patterns show single-phase compounds and are in agreement with published data.

The Mössbauer spectrometer is of the constant acceleration type and is equipped with a 10-mCi source of ^{57}Co diffused in a Rh matrix. The isomer shifts given in the text are referred to metallic iron.

3. Mössbauer Results

All the compounds studied are paramagnetic at room temperature and the Mössbauer spectra are either a symmetric or an asymmetric doublet due to the superposition of two symmetric doublets. The characteristics are reported in Table II. Figure 1 shows, for example, the case of TiFeGe.

By comparison with the other silicides, we may expect ^{57}Fe in TiMnSi to be on site I. The quadrupole coupling found in this case is 0.38 mm sec^{-1} which is greater than the value of 0.29 mm sec^{-1} found in the same structure for Fe_2P (*1*). It is difficult to compute the interatomic distances in TiMnSi because the position parameters x of the T and T' are unknown (*6*). If we use the x parameter of Fe(I) in Fe_2P, we compute the

TABLE II

MÖSSBAUER RESULTS

Compound	ε_1[a] (mm sec^{-1})	δ_1[b] (mm sec^{-1})	ε_2[a] (mm sec^{-1})	δ_2[b] (mm sec^{-1})	I_1/I_2
TiMnSi[c]	0.38	0.15			
TiFeSi	0.25	0.17	0.42	0.20	2
TiCoSi[c]	0.50	0.20	0.55	0.08	
TiNiSi[c]	0.50	0.25	0.41	0.06	
$MnFe_{0.5}Ni_{0.5}Si$	0.52	0.22			
NbFeSi	0.25	0.12			
TiFeGe	0.25	0.10	0.45	0.15	2
MnFeGe	0.70	0.30			
VCoSb[c]	0.32	0.25			
VFeSb	0.38	0.15			
TiCoSb[c]	0.40	0.20	—	0.02	

[a] Note quadrupole couplings (error ±0.02).

[b] Note isomer shifts relative to metallic iron (error ±0.05).

[c] The compounds without iron are assumed doped with 2% ^{57}Fe.

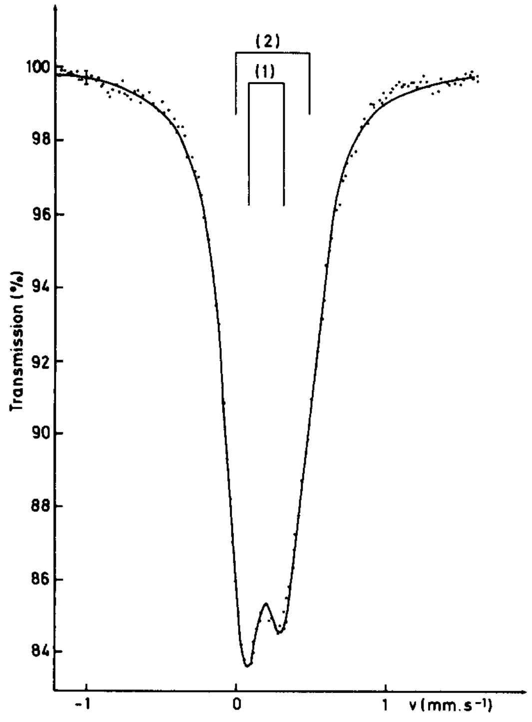

FIG. 1. Mössbauer spectrum of TiFeGe at 300°K; the solid line is the result of a least-squares fit with two doublets.

distances Fe(I)–Si(I) and Fe(I)–Si(II) to be equal to 2.33 and 2.50 Å, respectively. The four Si atoms form a tetrahedron which is more distorted than that found in Fe_2P and the quadrupole coupling is actually larger as expected from a point-charge model.

TiFeSi and TiFeGe crystallize in the same structure and are characterized by similar quadrupole couplings. We observe two types of Fe in the ratio 2/1 as expected from the crystallographic data. Nevertheless, the site with the less distorted environment as deduced from X-ray measurements seems to have the larger quadrupole coupling.

The three compounds TiNiSi, TiCoSi, and $MnFe_{0.5}Ni_{0.5}Si$ crystallize in the same orthorhombic structure with very similar lattice parameters and show very similar ε_1 values. The Fe atoms are expected to occupy site I as in TiFeSi. Nevertheless, in TiNiSi and TiCoSi, they occupy sites I and II of the orthorhombic structure, and sites II seem to have slightly different environments for both compounds. The population ratio of sites I and II in the Mössbauer spectra depends on the heat treatment of the samples, but we have never obtained the iron atoms entirely on sites I.

Suspecting the presence of an FeSi phase in our doped sample of TiNiSi and TiCoSi, we recorded the Mössbauer spectra at 573°K. No change was revealed. Had FeSi been present, its quadrupole coupling should have showed a noticeable decrease at 573°K (*7*). Another possibility was to have a CoSi or a NiSi phase containing a few percent of ^{57}Fe, but the quadrupole splittings of those phases are around 0.2 mm $\sec^{-1}$ (*8*, *9*) and are incompatible with our data. The presence of a TiSi phase seems very doubtful since the preparation methods of this compound are rather complicated (*10*).

In $MnFe_{0.5}Ni_{0.5}Si$, one type of Fe site is detected by Mössbauer spectroscopy and the hyperfine parameters are similar to those observed for iron in site I in the other compounds. Thus, we conclude that Fe is present in site I of $MnFe_{0.5}Ni_{0.5}Si$. A quenched sample of this compound (*11*) was found to be ferromagnetic with $T_C = 393$°K. Our sample, which was not quenched, is paramagnetic down to 77°K. The magnetic properties of this compound seem very sensitive to the preparation and probably to the stoichiometry of the sample.

NbFeSi, which has also the TiNiSi structure (*12*), is characterized by a single doublet with a small quadrupole coupling amounting to 0.21 mm $\sec^{-1}$.

TiCoSb, VCoSb, and VFeSb, which have the cubic structure of MgAgAs, have very similar Mössbauer parameters. Only one type of iron is observed in VCoSb and VFeSb. Since VCoSb is ordered (cf. Table I), we conclude that iron normally substitutes for Co in site III. In TiCoSb, Fe is on two sites replacing Co and Ti. The Ti site is characterized by a zero-value quadrupole splitting in agreement with the high symmetry of this site. At 77°K, there is no evidence of magnetism for these antimonides even for VCoSb (*4*).

In MnFeGe, Fe occupies site I of Ni_2In structure and has a rather large quadrupole coupling, which is probably due to the low symmetry of site I of Ni_2In. A set of low-temperature spectra were recorded on MnFeGe. So far, we can only say that a magnetic structure shows up already at 250°K but it has been impossible to analyze it. This is compatible with the Curie temperature of 241°K observed by neutron diffraction (*13*). The small internal magnetic field of about 70 kOe is in agreement with the small magnetic moment on Fe atoms (0.38 μ_B) (*13*). Mössbauer data about MnFeGe have already been published (*14*) but the sample does not seem to be a single phase.

4. Conclusions

Preliminary Mössbauer results have been obtained on ternary silicides, germanides, and antimonides of transition metals.

As in the phosphides (*1*), the isomer shifts are small, even smaller in the compounds studied here. From the graph of Walker *et al.* (*15*), we may deduce a rather large 4*s* contribution, if we compute the number of outer electrons as done for the phosphides (*16*). We are led to postulate covalent bonding orbitals between metallic atoms and Si, Ge, or Sb.

Since the observed isomer shifts are similar to those of the phosphides (*1*), these compounds are expected to have a metallic character. Thus, the observed quadrupole couplings result from the sum of a lattice term and an electronic term which have opposite signs (*17*). This explains the small values of the quadrupole couplings and the absence of a systematic correlation between the absolute value of the quadrupole coupling and the distortion of the lattice. In these compounds, the conduction electrons seem to play a significant role. Except for MnFeGe, no magnetic spectrum has been observed down to 77°K.

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References

1. M. Wautelet, A. Gerard, and F. Grandjean, *J. Phys.* **38**, 29 (1977).
2. V. Johnson and W. Jeitschko, *J. Solid State Chem.* **4**, 123 (1972).
3. V. Johnson and W. Jeitschko, N.B.S. Special Publication 364, "Solid State Chemistry, Proceedings, 5th Materials Research Symposium," pp. 613–622 (1972).
4. M. Terada, K. Endo, Y. Fujita, and R. Kimura, *J. Phys. Soc. Japan* **32**, 91 (1972).
5. S. Rundqvist and F. Jellinek, *Acta Chem. Scand.* **13**, 425 (1959).
6. W. Jeitschko, *Met. Trans.* **1**, 2963 (1970).
7. G. K. Wertheim, V. Jaccarino, J. M. Wernick, J. A. Seitchik, H. J. Williams, and R. D. Sherwood, *Phys. Lett.* **18**, 89 (1965).
8. G. K. Wertheim, J. H. Wernick, and D. N. E. Buchanan, *J. Appl. Phys.* **37**, 3333 (1966).
9. I. A. Dubovtsev, F. A. Sidorenko, A. N. Bortnik, T. S. Shubina, and N. P. Filippova, *Phys. Status Solidi B* **49**, 405 (1972).
10. W. B. Pearson, "Handbook of Lattice Spacings and Structures of Metals," Vol. 2, p. 1254, Pergamon Press, Oxford (1967).
11. V. Johnson and C. G. Frederick, *Phys. Status Solidi A* **20**, 331 (1973).
12. W. Jeitschko, A. G. Jordan, and P. A. Beck, *Trans. Met. Soc. AIME* **245**, 335 (1969).
13. T. Suzuoka, E. Adelson, and A. E. Austin, *Acta Crystallogr. A* **24**, 513 (1968).
14. S. C. Bhargava and P. K. Iyengar, *Pramana* **2**, 126 (1974).
15. L. R. Walker, G. K. Wertheim, and V. Jaccarino, *Phys. Rev. Lett.* **6**, 98 (1961).
16. M. Wautelet, A. Gerard, and F. Grandjean, *J. Magn. Magn. Mater.* **5**, 78 (1977).
17. T. P. Das and D. K. Ray, *Phys. Rev.* **187**, 777 (1969).