Journal of Solid State Chemistry **151,** 313–316 (2000)
doi:10.1006/jssc.2000.8660, available online at http://www.idealibrary.com on IDEAL®

Hyperfine Interactions and Dynamic Characteristics of ^{119}Sn Dopant Atoms in $Ca_2Fe_2O_5$

I. G. Minyaylova, I. A. Presnyakov, K. V. Pokholok, A. V. Sobolev, and A. V. Baranov

Chair of Radiochemistry, Department of Chemistry, Moscow State University, 119899 Moscow V-234, Russia

G. Demazeau

Institut de la Chimie de la Matiere Condensee de Bordeaux, C.N.R.S., Avenue du Dr. A. Schweitzer, 33608 Pessac Cedex, France

and

G. A. Govor and A. K. Vetcher

Institute of Solid State Physics, Belarus

Received December 2, 1999; in revised form February 13, 2000; accepted February 18, 2000

^{119}Sn Mossbauer spectra of tin impurity ions located in the bulk of $Ca_2Fe_2O_5$ particles have been investigated over the 77–1070 K temperature range. This study has allowed us to determine the sign of electric field gradient (EFG) as well as the angle between directions of the main EFG axis and magnetic field induced at ^{119}Sn nuclei. The values obtained appear to be in a good accordance with distorted octahedral coordination of $^{119}Sn^{4+}$ ions. Analysis of the asymmetry of the ^{119}Sn quadrupole doublet at $T > T_N$ showed that the mean-square amplitudes of Sn^{4+} thermal vibrations along the EFG direction are greater than those in the perpendicular direction. The temperature behavior of the ^{119}Sn spectra is described in terms of the Debye model. © 2000 Academic Press

Key Words:

INTRODUCTION

Perovskite-type oxides, ABO_3, have been extensively studied due to their ability to stabilize cations in unusually high oxidation state (1), and the anion sublattice can accommodate a high concentration of anionic vacant sites (2). The $Ca_2Fe_2O_5$–ferrite is one of a series of compounds with the general formula $ABO_{2.5}$ which are derived from the perovskite structure by the introduction of an ordered array of oxygen vacancies. This compound has a brownmillerite-type structure, which is derived from the cubic perovskite structure ABO_3 by removing one-half of the oxygen atoms located along the [101] directions from the alternate (010) planes. A slight shift of iron atoms in the (0*k*0) planes leads to the formation of an orthorhombic structure with alternating layers of distorted (FeO_6) octahedra and (FeO_4) tetrahedra perpendicular to the *b* axis (3). $Ca_2Fe_2O_5$ is an antiferromagnet with a G-type magnetic structure (3). Strong superexchange interactions of the Fe^{3+} cations located in the oxygen octahedra (Fe_o^{3+}) and tetrahedra (Fe_t^{3+}) are antiferromagnetic both within like planes and between neighboring planes.

To obtain additional information on the local structure of dicalcium ferrite, hyperfine interactions on nuclei of diamagnetic ^{119}Sn atoms, introduced into the structure of $Ca_2Fe_2O_5$ in small amounts, were first studied in (4). It was shown that below the magnetic ordering temperature ($T < T_N$) ^{119}Sn spectra showed a magnetic hyperfine splitting pattern. It was assumed that the Sn^{4+} dopant cations occupy only octahedral cationic positions in brownmillerite-type structure of $Ca_2Fe_2O_5$. However, relationship between local structure and hyperfine parameters of ^{119}Sn atoms within $Ca_2Fe_2O_5$ still remained unclear. The present paper describes the results of a wide-range temperature investigation of $^{119}Sn^{4+}$ hyperfine interactions allowing us to characterize its local structure and dynamic properties in the lattice of $Ca_2Fe_2O_5$.

EXPERIMENTAL

The synthesis of $Ca_2Fe_2O_5$ samples containing 1 at.% ^{119}Sn dopant has been performed using the following procedure. At the first stage, iron and tin hydroxides were coprecipitated from an acid solution of Fe(III) and Sn(IV) stoichiometric mixture salts. Then, the hydroxides were washed with water, carefully dried at room temperature,

0022-4596/00 $35.00

and heated at 700°C in air to complete dehydratation. At the second stage, the stoichiometric mixture of the resultant ^{119}Sn doped iron oxide and calcium carbonate was ground thoroughly and annealed in air at 1200°C for several days.

The composition of the samples was confirmed by X-ray powder diffraction analysis (FR-552 focusing chamber monochromator with Cu$K\alpha_1$-radiation and Ge as internal standard), which was able to detect $Ca_2Fe_2O_5$ as the only phase with cell parameters coincident with those reported earlier (3).

The ^{119}Sn Mössbauer spectra were recorded over the 77–1070 K temperature range using a conventional constant acceleration Mössbauer spectrometer. The radiation sources $Ca^{119m}SnO_3$ and ^{57}Co(Cr) were kept at room temperature. All isomer shifts refer to the $CaSnO_3$ and α-Fe absorbers at 300 K.

RESULTS AND DISCUSSION

The ^{119}Sn Mossbauer spectra recorded at $T > T_N$ can be described as an asymmetric quadrupole doublet (Fig. 1a), characterized by the parameters $\delta = 0.01$ mm/s, $\Delta = 0.9 \pm 0.01$ mm/s. The full line-width at half-height for each component of a doublet ($\Gamma = 0.83 \pm 0.01$ mm/s, $T = 1070$ K) was found to be close to the correspondent value for the reference $CaSnO_3$ sample ($\Gamma = 0.85$ mm/s), which is evidence of equivalence of the crystallographic positions occupied by the doping Sn^{4+} cations. Since the tetravalent tin cations have isotropic electron configuration $3d^{10}4s^0$, the electric field gradient (EFG) observed at the $^{119}Sn^{4+}$ nuclei is due to the distortion of their crystallographic surroundings (lattice contribution). In the absence of any structural phase transitions (it is the case for $Ca_2Fe_2O_5$ (3)), the lattice contribution of the EFG ($q^{(1)}$) is nearly independent on temperature. This fact allowed us to use the quadrupole coupling constant ($e^2q^{(1)}Q = 2\Delta$) obtained from the spectra recorded at $T > T_N$ for calculating the hyperfine structure parameters corresponding to combined magnetic and quadrupole interactions at $T < T_N$.

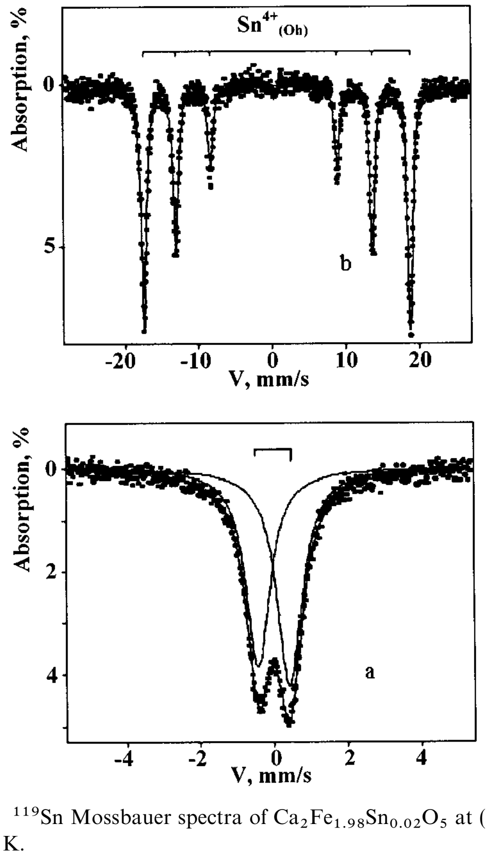

FIG. 1. ^{119}Sn Mossbauer spectra of $Ca_2Fe_{1.98}Sn_{0.02}O_5$ at (a) 1070 K and (b) 80 K.

The ^{119}Sn Mössbauer spectrum recorded at $T < T_N$ consists of one hyperfine splitting patterns reflecting combined quadrupole and magnetic interactions (Fig. 1b). The analysis of the spectrum, with fixed $|e^2q^{(1)}Q| = 1.8$ mm/s, enables one to determine the polar angle θ_{Sn} between the hyperfine field ($H = 287$ kOe, $T = 300$ K) direction and the principal axis system of the EFG. However, two different angles may be obtained depending on the sign of e^2qQ: 80 ± 7^0 ($e^2qQ < 0$) and 38 ± 7^0 ($e^2qQ > 0$). To eliminate this ambiguity, we have used the results of ^{57}Fe Mössbauer investigations of $Ca_2Fe_2O_5$ single crystals (6). In the referred work it was shown that for octahedrally coordinated Fe_o^{3+} cations $q^{(1)} > 0$ and $\theta_{Fe} = 78 \pm 10°$. Since the Sn^{4+} cations occupy the octahedral positions in the ferrite (4) and the H(^{119}Sn) direction is determined by magnetic moments of the nearest iron cations (7), it is obvious that, of the two values $\theta_{Sn} = 80°$ can be considered as a true angle (Fig. 2). This means that the sign of EFG at $^{119}Sn^{4+}$ nuclei is positive, as in the case of the Fe_o^{3+} cations. The same sign for the EFGs at the nuclei of two Mössbauer nuclides indicates a lack of considerable local distortions induced by the dopant atoms that seems to be reasonable because of close values of the ionic radii: $R(Sn_0^{4+}) = 0.69$ Å and $R(Fe_0^{3+}) = 0.65$ Å (8).

The additional information about the Sn^{4+} dopant atoms provided by low-temperature Mössbauer measurements can now be used for deconvoluting the spectra recorded in the paramagnetic region. The small width of the ^{119}Sn doublet components allows us to assume that the doublet asymmetry is not due to the superposition of a few independent quadrupole doublets with different isomer shifts. At the same time, the fact that the spectral asymmetry increases with an increase in temperature (from $A_</A_> = 0.96$ at $T = 760$ K to $A_</A_> = 0.82$ at $T = 1070$ K, where $A_<$ and $A_>$ stand for the absorption areas of the individual doublet components at lower and upper velocity, respectively) can be considered as evidence of the manifestation of the Goldanskii–Karyagin effect (9), associated with an anisotropy of the Sn^{4+} thermal vibrations in the $Ca_2Fe_2O_5$ structure. From the theory explaining this effect it follows that the area ratio of the $\pi(\pm\frac{1}{2} \to \pm\frac{3}{2})$ to $\sigma(\pm\frac{1}{2} \to \pm\frac{1}{2})$ transition

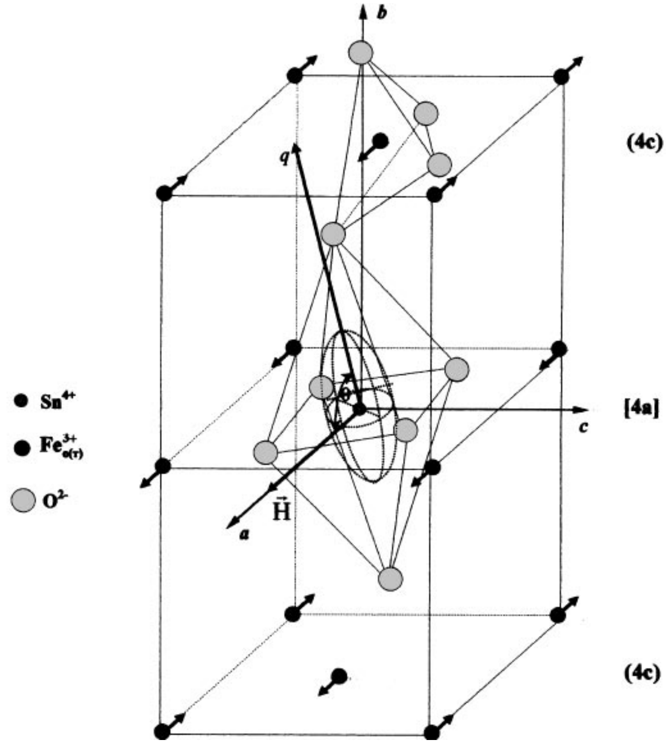

FIG. 2. Idealized fragment of the Sn^{4+} local environment in $Ca_2Fe_{1.98}Sn_{0.02}O_5$ structure (dotted lines show the orientation of the thermal ellipsoid of the doped tin ions).

probability is given by the expression (9)

$$\frac{A_\pi}{A_\sigma}=\frac{\int_0^1(1+u^2)\exp(-\varepsilon u^2)\,du}{\int_0^1(\frac{5}{3}-u^2)\exp(-\varepsilon u^2)du},$$

where $u=\cos\alpha$ (α is the angle between the EFG direction and the wave vector k), $\varepsilon=k(\langle x_\parallel^2\rangle-\langle x_\perp^2\rangle)$ ($\langle x_\parallel^2\rangle$ and $\langle x_\perp^2\rangle$ are the mean square amplitudes of vibration parallel and perpendicular to the EFG direction, respectively).

Taking into account $q^{(1)}(Sn^{4+})>0$, we determined the area ratio $A_\pi/A_\sigma=0.82\pm0.02$ at the highest temperature of measurements $T=1070$ K. Using this experimental value and numerical values of the integrals tabulated for different ε in [10], we calculated the difference $\langle x_\parallel^2\rangle-\langle x_\perp^2\rangle=1.21\times10^{-18}$ sm^2. The resulting positive value for $\varepsilon(Sn^{4+})/k$ is in accordance with the local crystallographic structure of unsubstituted ferrite, where tetragonally distorted oxygen octahedra are characterized by four short Fe_o^{3+}–O^{2-} distances in the basis plane ($R_\perp=1.96$ Å) and two elongated bonds ($R_\parallel=2.12$ Å) along the local fourfold axis, which is nearly coincident with the direction of the EFG at the Sn^{4+} nucleus (for the unsubstituted ferrite, the deviation is assessed at only ~8° (6) (Fig. 2)). It has been noted that the similar study of ^{57}Fe Mössbauer spectra is considerably complicated because of the superposition of the Fe_o^{3+} and Fe_t^{3+} quadrupole doublets with close parameters at temperatures above the ordering temperature (11).

In order to characterize the individual sites of the tin atoms, we examined the temperature dependence of the area (A) under the resonance curve for the spectra recorded at wide range temperature. The results obtained (Fig. 3) show that temperature dependence for logarithm of the ^{119}Sn spectra area is linear and well fitted by the relationship valid in the high-temperature Debye approximation (11)

$$\frac{d\ln(A)}{dT}=-\frac{3E_\gamma^2}{k_BMc^2\Theta_M^2},$$

where E_γ is the Mössbauer γ-ray energy, k_B is the Boltzmann constant, M is the atomic mass of ^{119}Sn, and c is the velocity of light.

The most important parameter which can be extracted from these results is the effective Mössbauer lattice temperature Θ_M averaged over the temperature range of the measurement. The slope observed, $d[\ln(A)]/dT=-2.81\times10^{-3}$K, corresponds to $\Theta_M=251\pm10$ K. To compare the $\Theta_M(Sn^{4+})$ value to that of matrix Fe^{3+} ions, we measured the temperature dependence of spectral areas for iron occupying octahedral (Fe_o) and tetrahedral (Fe_t) positions in the structure of $Ca_2Fe_2O_5$ (Fig. 4).

The obtained lattice temperature for iron ions ($\Theta_M^*(Fe_o^{3+})=350\pm30$ K and $\Theta_M^*(Fe_t^{3+})=360\pm30$ K) was found to be significantly greater than for tin probe atoms. The smaller value of $\Theta_M(Sn^{4+})$ implies therefore higher variational amplitudes for the tin ions in the temperature range investigated. Such a result is not surprising in view of the specific feature of the vibrational spectrum of the doping

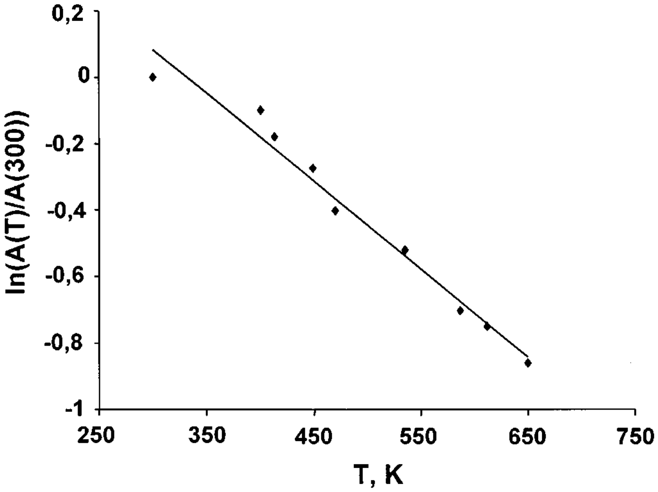

FIG. 3. Temperature dependence of the ^{119}Sn spectral area for $Ca_2Fe_{1.98}Sn_{0.02}O_5$.

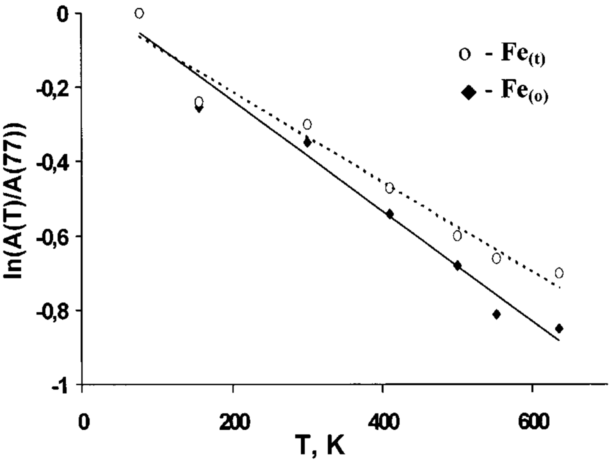

FIG. 4. Temperature dependence of the $^{57}Fe_{(o,t)}$ spectral area for $Ca_2Fe_{1.98}Sn_{0.02}O_5$.

atoms in crystals of ionic compounds. It was shown in (13) that given $M_i/M_m \gg 1$ (M_i and M_m are the masses of the impurity and the major component, respectively), the impurity atoms are involved in quasilocalized resonance vibrations whose frequencies are in the range of acoustic resonance frequencies of a perfect crystal. Such vibrations spatially localized on the impurity atom are characterized by a significantly increased amplitude and, hence, by low effective lattice temperature Θ_M, related to Θ_M^* of the matrix atoms by (13)

$$\Theta_M^* = \Theta_M \sqrt{\frac{M_i \xi_m}{M_m \xi_i}},$$

where ξ_i ($= \xi_{Sn}$) and ξ_m ($= \xi_{Fe}$) are the force constants of doping and matrix atoms, respectively. Assuming, to a first approximation, that $\xi_{Sn} \approx \xi_{Fe}$ and substituting the $\Theta_M(Sn^{4+})$ value in the above expression, we obtain $\Theta_M^* = 370 \pm 10$ K. This value is in good accordance with Θ_M^* directly obtained from the $A_{Fe}(T)$ dependence. It should be noted that a similar discrepancy in lattice temperatures determined from the spectra for diamagnetic impurity cations and the major component cations has been observed in (14) when studying α-Fe_2O_3 doped by ^{119}Sn. It was shown that the dynamic behavior of the Sn^{4+} impurity cations is adequately described in terms of the one-parameter Debye model with the effective Mössbauer temperature $\Theta_M(Sn^{4+}) = 350 \pm 20$ K. This value is significantly lower than $\Theta_M^*(Fe^{3+}) = 550 \pm 50$ K (14).

In conclusion, the comparative study of Mössbauer spectra of diamagnetic impurity ^{119}Sn atoms and paramagnetic ^{57}Fe atoms, which represent the major component of ferrite, showed that information extracted from the spectra of diamagnetic probes adequately describe the features of the crystallographic and magnetic structures of the compound under investigation. This result gives promise that diamagnetic probe Mössbauer spectroscopy can be successfully used in studying magnetically ordered compounds that do not contain Mössbauer atoms as major components.

ACKNOWLEDGMENT

This work was supported by the Russian Foundation for Basic Research.

REFERENCES

1. G. Demazeau, B. Buffat, M. Pouchard, and P. Hagenmuller, *J. Solid State Chem.* **45,** 88 (1982).
2. M. Takano, T. Okita, N. Nakayama, Y. Bando, Y. Takeda, O. Yamamoto, and J. B. Goodenough, *J. Solid State Chem.* **73,** 140 (1988).
3. S. Geller, R. W. Grant, and U. Gonser, *Prog. Solid State. Chem.* **5,** 1 (1978).
4. K. V. Pokholok, L. Fournes, G. Demazeau, and P. B. Fabritchnyi, *Solid State Commun.* **66,** 123 (1988).
5. J. C. Grenier, M. Pouchard, and R. Georges, *Mater. Res. Bull.* **8,** 1413 (1973).
6. R. W. Grant, *J. Chem. Phys.* **51,** 1156 (1969).
7. A. S. Moskvin, N. S. Ovanesyan, and V. A. Trukhtanov, *Hyp. Int.* **5,** 13 (1977).
8. R. D. Shannon, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
9. S. V. Karyagin, *Dokl. Akad Nauk SSSR* **148,** 1102 (1963).
10. P. A. Flinn, S. L. Ruby, and W. L. Kenl, *Science* **143,** 1434 (1964).
11. A. Colville, *Acta Crystallogr. Sect. B* **26,** 429 (1970).
12. F. Menil, *J. Phys. Chem. Solids* **46,** 763 (1985).
13. Yu. M. Kagan and Ya. A. Iosilevskii, *Zh. Eksp. Teor. Fiz.* **42,** 269 (1961).
14. E. Realo and A. Linn, *Izv. Akad. Nauk Est. SSR* **23,** 166 (1974).