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MAGNETIC HYPERFINE INTERACTION IN NiMnSb

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From an investigation of the Mössbauer effect in NiMnSb, the magnetic field on the diamagnetic antimony atoms is determined, and the magnetic moment of the excited state of ^{121}Sb is evaluated ($\mu = 2.45 \pm 0.02$ nm). X-ray diffraction studies together with a study of the anomalous dispersion of the scattering power of Ni and Mn were performed with the aim of elucidating possible mechanisms by which the effective magnetic field is created. The arrangement of atoms was determined, and the alloy was found to belong to the space group $T_d^2(F\bar{4}3m)$, the antimony atoms being situated within regular tetrahedra formed by the nickel atoms.

INTRODUCTION

DIFFICULTIES in calculating the contributions of different mechanisms bring about the situation that the existing models explain only qualitatively the magnitudes of the local magnetic fields at the diamagnetic atoms in magnetically ordered crystals.[1] Of great interest in this connection are investigations of the hyperfine fields in ferromagnetic alloys containing antimony.

The isotope ^{121}Sb has rather recently been introduced into the practice of laboratory investigations by nuclear gamma resonance.[2]

Earlier, we reported the discovery of strong magnetic fields at the ^{121}Sb nuclei in substituted yttrium iron garnet $Y_{2.5}Ca_{0.5}Sb_{0.25}Fe_{4.75}O_{12}$. In this case there is no contribution to H_{eff} from conduction electrons, and the high magnitude of the hyperfine field is due to superexchange interaction along the chain $Fe \rightarrow O \rightarrow Sb \rightarrow O \rightarrow Fe$,[3] which gives rise to a spin polarization of the ionic residue of the antimony atoms.

Until now the Mössbauer effect has been used to measure the magnetic fields at ^{121}Sb nuclei only in the compound MnSb, solid solutions of antimony in iron and nickel, and the iron spinels $Ni_{1-2x}Fe_{2-3x}Sb_xO_4$.[4-6] Further investigations in this direction will provide data for explaining the local magnetic fields at diamagnetic atoms.

The alloy NiMnSb was synthesized by Castelliz,[7] who established that it is ferromagnetic with a Curie temperature of 450 °C and its magnetism is due to magnetic moments localized on the Mn atoms. In this work Castelliz assumed the space groups T_d^2 or O_h^5 for the lattice of the alloy NiMnSb and noted that, as a consequence of the small difference in scattering ability of Ni and Mn atoms, it could not be determined whether their arrangement in the structure was a regular one.

PREPARATION OF SAMPLES AND EXPERIMENTAL METHOD

The intermetallic compound NiMnSb was obtained by melting in an induction furnace. The charge, which contained the stoichiometric proportions of the metals, was melted in a tantalum crucible in an argon atmosphere. The purity of the initial materials was: Ni—99.99%, Mn—99.98%, Sb—99.99%. After preparation, the melt was broken up in an agate crucible, re-mixed, and remelted. Then the ingot, together with the tantalum crucible, was placed in a quartz ampoule evacuated to a pressure of 5×10^{-5} Torr, kept at 750 °C for two weeks, and then gradually cooled. The melt after such treatment had coarse, uniform crystals over its surface. Control Debyegrams of powder obtained from different parts of the boule were identical, and the lines on them corresponded to a single phase.

The method of x-ray diffraction for determining the structure of the alloy and the distribution of Ni, Mn, and Sb atoms according to a regular system of points is similar to the one we previously described.[8]

Mössbauer spectra were taken in a spectrometer with electrodynamic vibrator working in the time domain.[9] One of the features of experiments with the isotope ^{121}Sb is the slow rate of counting the resonant γ-quanta, which makes more stringent requirements on the stability of the motion system and the system for registration of the γ-quanta. Control of the motion system was carried out without stopping the recording of the spectrum. To this end a second system of registration was used, which periodically measured the control resonance spectrum of a sample of ion oxide Fe_2O_3, the Doppler shift of which was produced at the opposite end of the vibrator rod. Drift of the values of the calibrating constant speed did not exceed 0.25 of the channel in the region of speeds ± 3 cm/s during the course of an experiment. The detector of the resonant γ-quanta was a scintillation counter (a crystal of NaI–Tl of thickness 0.2 mm and a photomultiplier FÉU-35A). Registration of the radiation with energy 37.2 keV was accomplished according to the "peak of flight." A thin copper foil was placed in front of the detector to improve the signal-to-noise ratio. As the source of resonant γ-quanta the isotope ^{121}Sn in the compound SnO_2 was employed.

EXPERIMENTAL RESULTS

The diffraction pattern of NiMnSb corresponds to a face-centered structure with space group O_h^5 or T_d^2. Absence of lines of an extraneous phase, which were observed by Castelliz,[7] was checked by registration at the points of corresponding portions of the diffractograms. The lattice parameter computed from the diffraction pattern, 5.900 ± 0.003 Å, together with the psychometric density, 7.60 g/cm^3, corresponds to 12 atoms in the elementary cell.

For K_α radiation of iron, cobalt, nickel, and copper anodes we carried out a theoretical computation of the diffraction patterns, with account taken of anomalous scattering, for different variants of the distribution of Ni, Mn, and Sb in a regular way among the points of the structures O_h^5 and T_d^2. An analysis of the relative intensities of the experimental diffraction maxima obtained in the above radiations and their comparison with the theoretical computations permitted a unique determination of the arrangement of atoms in the structure of the compound. As a result it was established that the distribution of Ni, Mn, and Sb atoms in the lattice of the alloy is ordered and described by the space group $T_d^2 \times (F\bar{4}3m)$. If the Sb atoms occupy the positions ($^3/_4$, $^3/_4$, $^3/_4$; $^1/_4$, $^1/_4$, $^3/_4$; $^1/_4$, $^3/_4$, $^1/_4$; $^3/_4$, $^1/_4$, $^1/_4$), then the atoms of Ni and Mn occupy respectively the positions (0, 0, 0; 0, $^1/_2$, $^1/_2$; $^1/_2$, $^1/_2$, 0; $^1/_2$, 0, $^1/_2$) and ($^1/_4$, $^1/_4$, $^1/_4$; $^3/_4$, $^3/_4$, $^1/_4$; $^1/_4$, $^1/_4$, $^3/_4$; $^1/_4$, $^3/_4$, $^3/_4$).

The Mössbauer spectrum of the compound NiMnSb measured at 100°K (Fig. 1) is symmetrical with respect to the center of gravity, which is evidence for the absence of quadrupole splitting. The magnetic hyperfine interaction evokes a splitting of the ground level of ^{121}Sb into $2I(^5/_2) + 1 = 6$ and of the excited level into $2I(^7/_2) + 1 = 8$ levels, between which the selection rules allow 18 transitions. The experimentally observed spectrum is a group of four lines of almost equal intensities and weak lines at each side. To determine the effective magnetic field and magnetic moment of the excited state we calculated the theoretical spectra, sums of 18 Lorentzian lines each of which was defined by three parameters: intensity, width, and position. The spectrum is a function of the effective magnetic field H, linewidth Γ, and the ratio of the g factors of the excited and ground states of the isotope ^{121}Sb, $R = g(^7/_2)/g(^5/_2)$. We chose the limits of variation of H on the basis of the nuclear magnetic resonance data,[10] that of R according to the investigations,[4,5] and the range of Γ from measurements of the resonance spectra of InSb of different thicknesses.

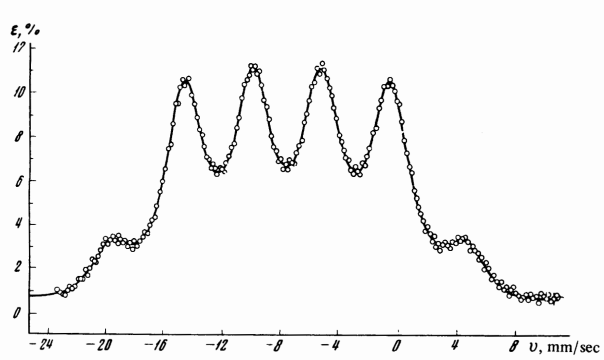

FIG. 1. Mössbauer spectrum of the compound NiMnSb (T = 100°K). Solid line–theoretical calculation for H = 290 kOe, Γ = 3.02 mm/s, R = 0.520. The magnitude of the effect ε is plotted as ordinate, and the rate of motion of the absorber relative to the $^{121}SnO_2$ source is plotted as abscissa.

The choice of theoretical parameters which gave the best agreement with the experimental spectrum was H = 290 Oe, Γ = 3.02 mm/s, R = 0.520. The results of the measurements of the resonance spectrum at room temperature correspond to H = 275 kOe, Γ = 3.02 mm/s, R = 0.520.

DISCUSSION

The results of the x-ray investigation of the alloy NiMnSb are illustrated in Fig. 2. The antimony atoms are arranged inside of tetrahedra formed by nickel atoms; the successive coordination spheres are occupied by six manganese atoms and twelve antimony atoms. The point group is $\bar{4}3m$.

As is known,[11] the elements of symmetry of any physical property of the crystal must include the elements of symmetry of the point group of the crystal. On the other hand, the electric field gradient as a property described by a second-rank tensor has a center of symmetry. Thus, the characteristic surface of second order the equation for which contains as many independent coefficients as there are independent components in the symmetrical tensor of the second rank, is in our case a sphere. Only in the case of sphere can the characteristic have four three-fold axes. From this it follows that the distribution of electrical charge around the antimony nuclei is spherically symmetrical, and in the hyperfine Hamiltonian there are no quadrupole terms.

It is of interest to compare the results of the experiment with the data of earlier investigations. In [7] it was supposed that the magnetic moment was localized on the Mn atoms. The interpretation of the authors of [12] was based on the conclusion that in the first coordination sphere of antimony are found manganese atoms and that the hyperfine field on the antimony nuclei is due mainly to the spins of these atoms. However, our x-ray investigations show that nickel atoms are in the first coordination sphere.

The values of the effective magnetic fields at 100 and 296°K presented above fit the $T^{3/2}$ law quite well and agree with the NMR data. The isomeric shift of the Mössbauer line in NiMnSb is −7.6 ± 0.2 mm/s relative to $^{121}SnO_2$, which is evidence for the metallic character of the bond.

The effective magnetic field at the antimony nuclei is evidently due to indirect exchange mechanism via polarization of the conduction electrons.[13]

For the magnetic moment of the excited state, using $\mu(^5/_2) = 3.359 \pm 0.001$ nm,[14] we obtain $\mu(^7/_2) = 2.45 \pm 0.02$ nm. This value differs from data of earlier investigations,[4,5] in which MnSb was used to determine the magnetic moment; the effective magnetic field in

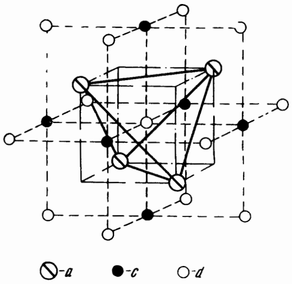

FIG. 2. Immediate surroundings of the antimony atoms in the alloy NiMnSb.

this compound is sufficient to create an experimentally observable Zeeman splitting on the ^{121}Sb nuclei. However, MnSb has hexagonal structure of the NiAs type, so that the hyperfine Hamiltonian contains a quadrupole term due to the presence of an electric field gradient arising as a result of the deviation of the surroundings of the antimony nuclei from cubic symmetry. In the presence of significant differences in the values of the quadrupole moments of the excited states[15] this circumstance creates additional difficulties. It has been recently shown that the magnetic moment of the alloy MnSb depends strongly on the composition of the alloy and its thermal history.[16] This obviously explains the discrepancies between our results and those of [4,5].

CONCLUSIONS

The x-ray and Mössbauer investigations of the alloy NiMnSb lead to the following conclusions:

1. The alloy crystallizes in an ordered structure with space group $T_d^2(F\bar{4}3m)$. If the Sb atoms are at $(\tfrac{3}{4}, \tfrac{3}{4}, \tfrac{3}{4}; \tfrac{1}{4}, \tfrac{1}{4}, \tfrac{3}{4}; \tfrac{1}{4}, \tfrac{3}{4}, \tfrac{1}{4}; \tfrac{3}{4}, \tfrac{1}{4}, \tfrac{1}{4})$, then the Ni and Mn are respectively at $(0, 0, 0; 0, \tfrac{1}{2}, \tfrac{1}{2}; \tfrac{1}{2}, \tfrac{1}{2}, 0; \tfrac{1}{2}, 0, \tfrac{1}{2})$ and $(\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4}; \tfrac{3}{4}, \tfrac{3}{4}, \tfrac{1}{4}; \tfrac{3}{4}, \tfrac{1}{4}, \tfrac{3}{4}; \tfrac{1}{4}, \tfrac{3}{4}, \tfrac{3}{4})$.

2. The magnitude of the effective magnetic field is 290 ± 10 kOe at $T = 100°$K and 275 ± 10 kOe at $T = 296°$K. The magnetic moment of the excited state of the isotope ^{121}Sb with spin $\tfrac{7}{2}_{+}$ is 2.45 ± 0.02 nm.

3. The isomeric shift of the compound relative to $^{121}SnO_2$ is -7.6 ± 0.2 mm/s, which corresponds to an electron density at the antimony nuclei $|\psi(0)|^2/a_0^3 = 16$.

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49