# Induction of strong magnetic fields at the nuclei of diamagnetic tin atoms in chalcogenide spinels

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(Submitted December 3, 1974)
ZhETF Pis. Red. **21**, No. 2, 132–135 (January 20, 1975)

Very strong magnetic fields $H^{Sn}$ (more than half a million oersteds), exceeding by almost an order of magnitude the values of $H^{Sn}$ in the analogous oxygen spinels, were observed at the nuclei of impurity diamagnetic tin atoms introduced into chalcogenide chromite spinels $CuCr_5S_4$, $CuCr_2Se_4$, $FeCr_2S_4$, and $CoCr_2S_4$. The signs of the fields $H^{Sn}$ were determined. It is shown that an appreciable contribution to $H^{Sn}$ is made by the intrasublattice $B-B$ interactions.

We report here observation of very strong (more than half a millon oersteds) magnetic fields at the nuclei of diamagnetic tin ions in ternary chalcogenides with spinel structure, exceeding by almost one order of magnitude the fields known for oxygen spinels.

The problem of induction of magnetic fields at nuclei of diamagnetic atoms in magnetic dielectrics and semiconductors has attracted much interest of late, since this problem touches upon fundamental questions in exchange interaction, delocalization, and distribution of the spin density in magnetic crystals.

In contrast to oxygen ferrimagnets, where this effect was observed and investigated heretofore, chalcogenides with spinel structure $AB_2X_4$, where ($X =$ S, Se, or Te, and $A$ and $B$ are metal ions) exhibit a great variety of magnetic and electric properties in one class of substances. Among the chalcospinels one encounters ferro-, ferri-, and antiferromagnets, and their conductivity can range from semiconducting to metallic.[1]

We investigated the Mössbauer spectra of $Sn^{119}$ nuclei. The tin was introduced into the chromite spinels $CuCr_2S_4$, $CuCr_2Se_4$, $FeCr_2S_4$, and $CoCr_2S_4$ (see the table for the detailed compositions). The technology of sample production is described in[2].

| Compound | $H^{Sn}$, kOe |
|---|---|
| $CuCr_{1.95}Sn_{0.05}S_4$ [1] | $+ 530 \pm 10$ |
| $CuCr_{1.9}Sn_{0.1}Se_4$ | $+ 490 \pm 10$ |
| $Fe_{1.1}Cr_{1.8}Sn_{0.1}S_4$ | $- 470 \pm 15$ |
| $Co_{1.1}Cr_{1.8}Sn_{0.1}S_4$ | $- 405 \pm 20$ |

[1] Sekizawa and co-workers[10] recently reported an investigation of the hyperfine fields at tin in $CuCr_2S_4$. He obtained at 78°K a value $H^{Sn} = 580$ kOe, which agrees in order of magnitude with our data. Some differences between the field values may be due to the different technologies used to produce the samples.
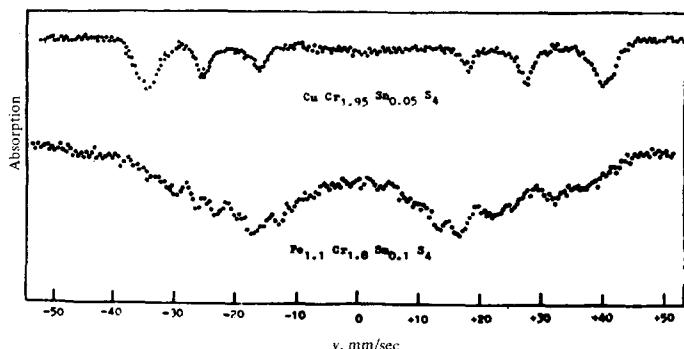
Mössbauer spectra of $Sn^{119}$ nuclei in the chalcogenide spinels $CuCr_{1.95}Sn_{0.05}S_4$ (upper spectrum) and $Fe_{1.1}Cr_{1.8}Sn_{0.1}S_4$ (lower spectrum) at 78 °K.

The first two compounds (copper chromites) are ferromagnets with metallic conductivity; $T_c = 420$ °K for the sulfide and $T_c = 460$ °K for the selnide.[3] $FeCr_2S_4$ and $CoCr_2S_4$ are ferrimagnets with collinear magnetic structure[5] and semiconductor conductivity.[6] Their Curie temperatures are 180 and 235 °K, respectively.[7]

In the paramagnetic temperature region, the Mössbauer spectra of $Sn^{119}$ constitute, for all samples, a single line of width 1.4–1.5 mm/sec and an isomer chemical shift $\delta = +1.3$–1.4 mm/sec (relative to $SnO_2$). This value of the shift differs greatly from the value of $\delta$ in oxygen ferrimagnets[8,9] (where it is close to zero), and points to a strong covalence of the chemical bond of the metal ion with the chalcogen (and to an increase in the electron density in the region of the $Sn^{119}$ nuclei).

Figure 1 shows the spectra of the $Sn^{119}$ nuclei for the spinels $CuCr_2S_4$ and $FeCr_2S_4$ at 80 °K. Attention is called to the unusually large magnetic hyperfine splitting of the spectra. The spectra of the copper spinels are well resolved, but the lines are strongly broadened ($\Gamma \approx 4$ mm/sec for the outermost lines). In the copper spinels, and particularly the iron spinels, one can note an additional splitting of the lines into components; this indicates that the tin ions have several nonequivalent positions. The table lists the mean values of the effective magnetic fields $H^{Sn}$ at the tin nuclei.

We note that in oxygen spinels the magnetic field at the tin nuclei fluctuates approximately in the range from 50 to 200 kOe.[11,12] The hitherto known strongest field $H^{Sn}$ in oxygen ferrimagnets is that of lanthanum orthoferrite[9] ($H^{Sn} = 260$ kOe). Thus the fields $H^{Sn}$ observed in chalcogenide spinels are several times stronger than the fields in all the known oxygen ferrimagnets.

An interesting result was obtained by measuring the Mössbauer spectra in an external magnetic field of 20 kOe. It turned out that the field $H^{Sn}$ in the spinels $Cu[Cr_2]X_4 (X = S, Se)$ is positive, i.e., its direction coincides with the direction of the magnetic moment of the sample. In the ferrimagnetic spinels $Co[Cr_2]S_4$ and $Fe[Cf_2]S_4$ the sign of the field $H^{Sn}$ is negative, i.e., the field at the tin is directed opposite to the overall magnetization of the sample and coincides in direction with the moment of the $A$-sublattice.

Two points are of interest here: first, the copper ions

in the chromites $CuCr_2S_4$ and $CuCr_2Se_4$ are nonmagnetic.[13,14] Therefore the total field at the tin nucleus ($\sim 500$ kOe) is produced entirely by the chromium ions via the intrasublattice $B$-$B$ interaction (the tin ions are in the $B$ sublattice).[12] The positive sign of the field $H^{Sn}$ in these spinels indicates that the spin of the $3d$ electron transferred from the chromium ions to the $5s$ shell of the tin ions is oriented parallel to the magnetic moment of the $Cr^{3+}$ ions. Second, the negative sign of the field at the tin in the spinels $FeCr_2S_4$ and $CoCr_2S_4$ indicates that the field produced by the intersublattice interaction $A$-$X$-$B$ exceeds in absolute value the contribution from the $B$-$B$ interaction. The spin of the $3d$ electron transferred from Fe (Co) to the tin ion via the $A$-$X$-$B$ bond coincides in direction with the moment of the $Fe^{2+}$ ($Co^{2+}$) ion.

It if is assumed that the contribution made to the field $H^{Sn}$ by the $B$-$B$ interaction is approximately same in the copper chromites and in the spinels $FeCr_2S_4$ and $CoCr_2S_4$, then we can estimate roughly the contribution made to the field $H^{Sn}$ by the intersublattice $A$-$X$-$B$ interaction. For example, in the spinel $FeCr_2S_4$ we have approximately $H^{Sn} = H^{Sn}_{A-X-B} + H^{Sn}_{B-B}$, and $H^{Sn}_{A-X-B} = -470$ kOe $-530$ kOe $= -1000$ kOe.

Such gigantic magnetic fields at the nuclei of diamagnetic atoms appear to be due to the appreciable overlap of the atomic orbitals $Sn$-$X$ and $X$-$Fe(Cr)$, i.e., to the strong covalence that is typical of chalcogenide compounds.

More detailed data on these compounds will be published by us in the near future.

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# Erratum: Induction of strong magnetic fields at the nuclei of diamagnetic tin atoms in chalcogenide spinels [JETP Lett. 21, No. 2, 59–60 (January 20, 1975)]

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ZhETF Pis. Red. 21, No. 11, 692 (June 5, 1975)

Page 59, lines 3 and 4 of the table should be interchanged in the Compound column. On p. 50, right-hand column, line 22 from the top, read "... the spinel $CoCr_2S_4...$" instead of "...the spinel $FeCr_2S_4...$"