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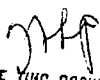
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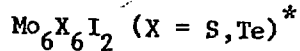
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**MASTER**

<sup>127</sup>I " MOSSBAUER STUDY OF CHEVREL-PHASE SUPERCONDUCTORS



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The Chevrel-phase compounds  $\text{Mo}_6\text{X}_6\text{I}_2$  (X = S, Te) exhibit very interesting superconducting behavior. The transition temperatures dramatically increase in both  $\text{Mo}_6\text{X}_8$  structures by replacing 2 of the X atoms with iodine atoms. This enhancement in superconducting behavior is closely related to the number of electrons on the  $\text{Mo}_6$  cluster in these compounds. The iodine atoms in these compounds preferentially occupy the 2c sites while the remaining X atoms occupy the 6f sites. We have performed the Mössbauer effect measurements using the 57.6-keV transition in <sup>127</sup>I to evaluate the charge on the iodine. Assuming the charge on S to be -2, the experimental value of nearly -1 charge on iodine leaves 22.3 electrons per  $\text{Mo}_6$  cluster which is close to that predicted in  $\text{SnMo}_6\text{S}_8$ . This accounts for the high  $T_c$  of  $\text{Mo}_6\text{S}_6\text{I}_2$  (which is close to that of  $\text{SnMo}_6\text{S}_8$ ).

In  $\text{Mo}_6\text{Te}_6\text{I}_2$ , assuming Te to have nearly -1 charge, we obtain 28.3 electrons per  $\text{Mo}_6$  cluster. The observation of superconductivity in this compound then reflects a significantly distinct band structure of tellurides compared to those of sulphides.

The quadrupole interactions at the iodine nucleus in  $\text{Mo}_6\text{S}_6\text{I}_2$  and  $\text{Mo}_6\text{Te}_6\text{I}_2$  are small but have opposite signs signifying bonding differences between these compounds.

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## INTRODUCTION:

The Chevrel phase compounds  $MMo_6X_8$  exhibit very interesting physical properties.<sup>1</sup> When M is Fe or Cu and X is a chalcogen, one has superionic conductors. Changing M to Sn or Pb, for example, one observes superconductivity. If M is a magnetic rare-earth atom one can have reentrant superconductivity or antiferromagnetism.<sup>2</sup> In this paper we shall deal with the properties related to the superconductivity of iodine substituted  $Mo_6X_8$  compounds with  $X = S, Te$ .

It is now generally accepted that the superconductivity arises from the 4d electrons on the Mo clusters. Detailed band structure calculations show that the d-band has narrow structure near the Fermi level and its width is governed by the intercluster Mo-Mo separation.<sup>3-6</sup> The second parameter which is equally important is the number of d-electrons on the  $Mo_6$ -cluster. This is determined by the nature of M and X atoms in the structure, and their influence has been qualitatively ascribed to the charge transfer from M and X atoms to the cluster.<sup>1,7</sup>

In this paper we attempt to obtain experimentally the charge on iodine atoms in  $Mo_6X_6I_2$  ( $X = S, Te$ ) compounds from the  $M^{55}Co$  Mossbauer isomer shift and quadrupole interaction measurements. The estimate of charges on I and S will permit us to obtain the total number of electrons per  $Mo_6$  cluster and to correlate this to  $T_c$  variation in some of the Chevrel phase compounds (see Table I).

## EXPERIMENTAL:

The sample of Chevrel phase compounds  $\text{Mo}_6\text{X}_6\text{I}_2$  ( $\text{X} = \text{S}, \text{Te}$ ) were produced by standard powder metallurgical methods and the X-ray diffraction measurements indicated very small amount of  $\text{MoS}_2$  phase.<sup>7,8</sup> The superconducting temperatures of these and some other Chevrel phase compounds are given in Table I.<sup>1</sup>

The Mössbauer effect measurements were carried out using the 57.60 keV  $5/2 \rightarrow 7/2$  resonance transition in  $^{127}\text{I}$ . The monochromatic radiation was obtained from a ZnTe source. All the measurements were carried out using a conventional spectrometer and a helium cryostat.

## RESULTS AND DISCUSSION:

In Figure 1 we present the structure of  $\text{Mo}_6\text{S}_6\text{I}_2$  compound.<sup>8</sup> It is important to note that the iodine atoms do not substitute the sulphur atoms at random. They preferentially occupy the 2c sites with point symmetry 3. Figure 2 shows the Mössbauer spectrum of  $\text{Mo}_6\text{S}_6\text{I}_2$  and  $\text{Mo}_6\text{Te}_6\text{I}_2$  measured at 4.2 K. The spectra are slightly asymmetric showing the presence of a small quadrupole interaction. The values of the isomer shift and quadrupole interaction are presented in Table II.

The systematics of the isomer shift for the iodine compounds has been approximately described by the equation

$$S = 3.1 h_s - 0.50 h_p + 0.16$$

when measured with a ZnTe source.<sup>9</sup> Here  $h_s$  and  $h_p$  are number of localized 5s and 5p holes, S is the isomer shift in  $\text{mm s}^{-1}$ .

Within the experimental accuracy the isomer shifts for the two compounds are nearly equal. The quadrupole interaction on the otherhand has opposite sign (see Table II). The quadrupole interaction is a measure of the electric-field-gradient (EFG) at the nucleus produced by the lattice charges and by the hole in the 5p shell. An estimate of lattice contribution to the EFG indicates its contribution to the measured quadrupole interaction to be less than 50 MHz. Hence the measured quadrupole interaction represents primarily the 5p hole contribution.

In evaluating this data we have used the Townes and Dailey model.<sup>9</sup> The switch in the sign of the quadrupole interaction between the two compounds can be understood in terms of differing number of electrons in the iodine  $p_x$ ,  $p_y$  and  $p_z$  orbits. The p-electron unbalance defined by  $U_p = e^2qQ/(e^2qQ)_{\text{atom}}$  is equal to  $(-n_z + n_x)$  where  $n_z$  and  $n_x$  are populations of the p-orbitals along z and x direction and  $(e^2qQ)_{\text{atom}}$  is due to one p-hole. (2293 MHz). In  $\text{Mo}_6\text{S}_6\text{I}_2$ ,  $|n_z| > |n_x|$  while the situation will be reversed in  $\text{Mo}_6\text{Te}_6\text{I}_2$ .

In order to deduce the values of  $n_z$  and  $n_x$ , it is necessary to assume  $h_s = 0$  in the isomer shift expression. The resulting values are given in Table II. This also permits us to obtain the charge transfer to iodine.

From crystal chemistry arguments,<sup>7</sup> the charge on S, Se and Te in  $\text{Mo}_6\text{X}_8$  compounds is estimated to be -2.0, -1.75 and -1.33, respectively. The charge on S is confirmed from the band calculations.<sup>3,6</sup> Mössbauer experiments<sup>10</sup> on  $\text{Mo}_6\text{Te}_8$  indicate the local charge on Te to be -1.0. In both  $\text{Mo}_6\text{S}_6\text{I}_2$  and  $\text{Mo}_6\text{Te}_6\text{I}_2$ , the <sup>127</sup>I Mössbauer studies indicate iodine to have about -0.85

charge. This permits us to determine the valence electron concentration (VEC) per cluster of  $\text{Mo}_6$  atoms which are given in Table I. It is important to note that VEC value of 22 electrons produces highest  $T_c$ . In  $\text{SnMo}_6\text{S}_8$  the isomer shift of Sn indicates it to be a divalent atom,<sup>11</sup> thus contributing two 5p electrons to the 4d band of  $\text{Mo}_6$ -cluster. The  $T_c$  values for  $\text{SnMo}_6\text{S}_8$  and  $\text{Mo}_6\text{S}_6\text{I}_2$  are hence nearly equal inspite of slight differences in their structure. When 3+ valence rare-earths are substituted for the M atom, one has VEC of 23 electrons and the Fermi level shifts near a minimum in the density of states.

In the tellurides on the otherhand, the 3p levels are only partly occupied (unlike in the sulphides in which S has a valency of -2). This will lead to a situation with the Fermi level crossing the p-band or the p- and d-bands hybridizing. Due to this complication we do not expect the simple VEC rule to apply in tellurides. The concentration of 28 electrons produces semiconducting behavior in  $\text{Mo}_6\text{Te}_8$  while about the same concentration makes  $\text{Mo}_6\text{Te}_6\text{I}_2$  a superconductor. Similar conclusions were arrived at from the  $^{125}\text{Te}$  Mössbauer studies of  $\text{Mo}_6(\text{Te}_{1-x}\text{Se}_x)_8$  compounds.<sup>9</sup>

#### CONCLUSION:

The Mössbauer effect measurements in  $\text{Mo}_6\text{S}_6\text{I}_2$  and  $\text{Mo}_6\text{Te}_6\text{I}_2$  using the  $^{127}\text{I}$  resonance have been used to evaluate the superconducting behavior. The analysis of the isomer shift and the quadrupole interaction in these compounds have been used to deduce the valence electron concentration per  $\text{Mo}_6$ -cluster which is closely related to the value of  $T_c$ . Within this description telluride compound shows non-local p electron behavior.

The sign of the quadrupole interaction is opposite for the two compounds and has been related to different populations of the 5p-orbitals of iodine. The exact significance of this result is not yet understood.

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Table I

Valence electron concentrations (VEC) in  
some of the Chevrel phase compounds

Compound	$T_c$ °K	VEC/Mo <sub>6</sub> Cluster	Ref
Mo <sub>6</sub> S <sub>8</sub>	-	20	7
Mo <sub>6</sub> Se <sub>6</sub>	6.3	22	7
Mo <sub>6</sub> Te <sub>8</sub>	-	28	10
Mo <sub>6</sub> S <sub>6</sub> I <sub>2</sub>	14.0	22.3	This Work
Mo <sub>6</sub> Se <sub>7</sub> I <sub>1</sub>	7.6	22.75	7
Mo <sub>6</sub> Te <sub>6</sub> I <sub>2</sub>	2.6	28.3	This Work
Pb <sup>2+</sup> Mo <sub>6</sub> S <sub>8</sub>	15.2	22	7
Sn <sup>2+</sup> Mo <sub>6</sub> S <sub>8</sub>	14.0	22	7
RE <sup>3+</sup> Mo <sub>6</sub> S <sub>8</sub>	<2.0	23	7



Table II

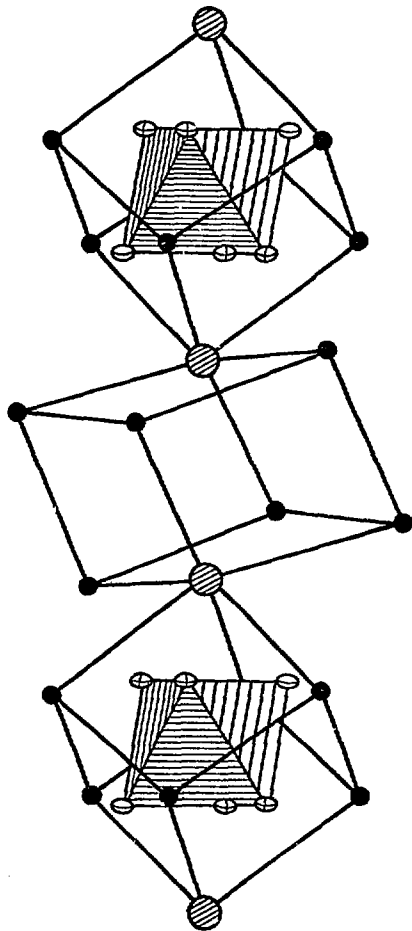
Isomer Shift, quadrupole interaction, occupancy of p orbitals,  
 $U_p$  and Charge transfer for iodine in Chevrel phase compounds

Compound	$S$ $\text{mms}^{-1}$	$e^2qQ$ MHz	$U_p$	$n_z$	$n_x$	Charge transfer per iodine
$\text{Mo}_6\text{S}_6\text{I}_2$	$0.0 \pm 0.1$	$-390 \pm 20$	-0.17	2.0	1.84	-0.84
$\text{Mo}_6\text{Te}_6\text{I}_2$	$0.1 \pm 0.1$	$+325 \pm 20$	+0.14	1.86	2.00	-0.86

## FIGURE CAPTIONS:

Fig. 1. Structure of  $\text{Mo}_6\text{S}_6\text{I}_2$  showing the preferential occupancy of iodine atoms.

Fig. 2. Mössbauer spectra of (a)  $\text{Mo}_6\text{S}_6\text{I}_2$  and (b)  $\text{Mo}_6\text{Te}_6\text{I}_2$  measured using the 57.6 keV resonance in  $^{127}\text{I}$  at 4.2 K.



- ⊖ I (2c)
- S (6f)
- ⊕ M<sub>0</sub>

