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THE MÖSSBAUER EFFECT IN COMPOUNDS OF THE FLUORITE TYPE ($IrSn_2$ AND $PtSn_2$)

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The resonance absorption of the 23.8-keV γ quanta by Sn^{119} nuclei in the compounds $IrSn_2$ and $PtSn_2$, which have the fluorite (CaF_2) structure has been studied over the temperature range from 77 to 600°K. The probabilities for recoilless resonance absorption of the γ quanta and the widths of the absorption lines have been determined for both compounds. The results are interpreted on the basis of data concerning the structure and the nature of the chemical bond in these compounds.

INTRODUCTION

THE successful use of the compound Mg_2Sn[1-3] as a source of 23.8-keV γ quanta showed that this compound has a marked temperature dependence of the probability for recoilless emission of γ quanta, so that in working with Mg_2Sn it must be put in a dewar at liquid nitrogen temperature. The chemical bond between the Mg and Sn is covalent in character, the saturation of the bond is achieved by forming an sp^3-hybrid, and magnesium stannide is a semiconductor.[4] The structure of the compound Mg_2Sn is the antiisostructure to CaF_2, in which the atoms of the more electronegative Sn occupy the positions of the electropositive element Ca.

It was shown theoretically by Yu. Kagan[5] that if the unit cell of a crystal contains two or more atoms the probabilities for resonance emission or absorption of γ quanta and their temperature dependence show certain peculiarities resulting from the appearance of optical branches in the vibration spectrum of the atoms of the crystal. For example if the interaction between the heavy atoms that are responsible for the Mössbauer effect is predominant, one may find a high probability for recoilless resonance absorption at high temperatures and a weak temperature dependence. In the case of Mg_2Sn the heavy Mössbauer atom Sn^{119} is surrounded by Mg atoms of lower mass, but the covalent bonding results mainly in interaction between atoms of different types so that, according to Yu. Kagan, for this case the contribution of the optical modes of vibration of the Sn atoms is considerably reduced. This result for Mg_2Sn was established in [1].

It is known that two compounds of tin crystallize in a structure of the CaF_2 type: $IrSn_2$ and $PtSn_2$,[6] which have metallic conductivity. In these compounds the Sn atoms are located at the sites of the F atoms. It was of interest to study, on a given type of crystal lattice, the effect of changing the surroundings of the Mössbauer atom, the mass of the atom, and the structure of the d-band. Thus the present investigation of the Mössbauer spectra of $IrSn_2$ and $PtSn_2$ is a natural extension of our earlier work[1] which also studied the causes that affect the line shape.

LINE WIDTHS AND PROBABILITY FOR RESONANCE ABSORPTION

The $IrSn_2$ and $PtSn_2$ compounds were obtained by melting the components in quartz ampoules in vacuum with subsequent annealing at 750°C for 50 hrs followed by slow cooling to room temperature. The x-ray photos, taken with iron radiation, confirmed the presence of the lines of only a single phase for both $IrSn_2$ and $PtSn_2$, with lattice parameters $a = 6.34$ Å and $a = 6.43$ Å, respectively.

The absorbers for studying the resonance absorption of γ quanta were prepared by pressing powders of the compounds in a mixture with beryllium oxide. Absorbers varying in thickness from 5 to 40 mg/cm^2 were prepared. The absorption spectra were measured on a cam-drive apparatus. The source of the 23.8-keV γ quanta was Mg_2Sn at liquid nitrogen temperature. The magnitude of the effect $\epsilon(\%)$ and the width of the absorption line at half maximum Γ_{exp} were determined for each absorber within the range of thicknesses cited. The

Compound	f'		Γ_{exp}, mm/sec	δ, mm/sec
	77° K	290° C		
$IrSn_2$	0,73±0.05	0.39±0.03	0.82±0.02	−0.05±0.02
$PtSn_2$	0,76±0.05	0.43±0,03	0.76±0.02	+0.35±0.02
Mg_2Sn	0.77±0.08	0.28±0.03	0.68±0.01	0.00

The values cited for Γ_{exp} are obtained by extrapolation to zero thickness.

dependence of the effect on temperature was measured for $IrSn_2$ and $PtSn_2$ with absorbers of the same thickness (12 mg/cm^2), using a specially prepared thermostat which allowed us to maintain the temperature to within 5° over the range from 77 to 650°K.

The probability f′ for recoilless resonance absorption of the γ quanta was determined by the same method as in the work with Mg_2Sn.[1] The results of the analysis of the Mössbauer lines for the $IrSn_2$ and $PtSn_2$ compounds are given in the table, with the values for Mg_2Sn given for comparison. The dependence of the resonance absorption effect on temperature was measured over the temperature interval cited above. Since the width Γ_a of the absorption line did not change noticeably with temperature, the computation of the effective absorber thicknesses and the values of f′ were done using the value of the observed effect and the dependence of ϵ on absorber thickness at room temperature and liquid nitrogen temperature. The errors in the determination of f′ cited in the table include the errors in our measurements, but errors in the lifetime and conversion coefficient[7] may increase the error in the absolute value of f′. Within the accuracy of the measurements, the value of Γ_{exp} was the same at 77 and 650°K. The isomer shifts given in the table are measured relative to the Mg_2Sn source.

Figure 1 shows the dependence of the resonance absorption probability on temperature for all three compounds of the fluorite type.

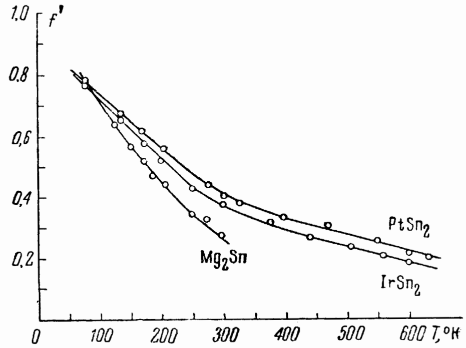

FIG. 1. Temperature dependence of probability for recoilless resonance absorption for $IrSn_2$, $PtSn_2$ and Mg_2Sn.

Since compounds of the fluorite type contain more than one atom in the unit cell, the vibration spectra of these crystals must contain, in addition to the acoustic phonon branches, higher-lying optical branches, which, according to the theory of Yu. Kagan,[5] are mainly responsible for determining f′ and its temperature dependence. According to this theory the value of f′ is the higher the greater the relative size of the vibration amplitude of the heavy Mössbauer atom in the high-lying optical branches. The amplitude of vibration of such an atom in the optical branches is determined by the nature of the chemical binding of the Mössbauer atoms in the lattice: the stronger the interaction, the greater the importance of the optical branches in vibrations of the heavy atom, the smaller the interaction the less their importance, and when they are absent the heavy atom practically does not vibrate at the frequencies of the optical branches. In the compound Mg_2Sn the Mg and Sn atoms form hybrid sp^3-bonds, which weakens the interaction of the Sn atoms. In this case the contribution of optical branches for the heavy Mössbauer atom Sn is considerably reduced, which results in a rapid drop in f′ with increasing temperature because of the excitation of acoustic phonons, and only at low temperatures, when the total number of phonons is small, is the role of the optical branches increased, resulting in a quite large value of f′ for Mg_2Sn.

As we see from Fig. 1, both compounds $IrSn_2$ and $PtSn_2$ have a weaker temperature dependence than Mg_2Sn. Thus, the dependence f′(T) can be explained qualitatively on the basis of the different chemical bindings in Mg_2Sn, $IrSn_2$ and $PtSn_2$. Whereas the binding forces in Mg_2Sn are mainly covalent, in $IrSn_2$ and $PtSn_2$ we have mainly metallic binding. Thus the interaction between atoms of the same kind becomes comparable with the interaction of different atoms. It is even possible that the interaction between the Sn Mössbauer atoms in $IrSn_2$ and $PtSn_2$ becomes predominant, which leads to an increased importance of the optical high-lying vibrations in the vibration spectra of these compounds as compared to Mg_2Sn.

In accordance with this, f′ for the $IrSn_2$ and $PtSn_2$ compounds falls off more slowly with temperature than for Mg_2Sn. The slight difference in mass of the Ir and Pt atoms has an effect on the temperature dependence of f′; for the $PtSn_2$ compound with the heavier Pt the falloff with temperature is slower.

Despite the fact that the temperature dependence of f′ is weaker for $IrSn_2$ and $PtSn_2$ than for Mg_2Sn, one cannot recommend these compounds as sources:

their line widths are much greater than Γ_{exp} for Mg_2Sn. We know that in cubic crystals with high symmetry of the surroundings of the Sn atom, we should find a Mössbauer line with the natural width. The broadening of the Mössbauer lines in $IrSn_2$ and $PtSn_2$ may be due primarily to the following causes. First, the Sn atom in these compounds is in a tetrahedral surrounding, whereas in Mg_2Sn it is at the center of a cube of Mg atoms. But in metallic compounds of this type it is difficult to claim a preferential deformation of the electron cloud leading to anisotropy of the electric field gradient at the nucleus of the Sn atom. Therefore we must regard as primary the second cause of broadening of the Mössbauer line in these compounds—the presence in the lattice of the paramagnetic atoms Ir and Pt, which produce a sizable effective internal magnetic field at the Sn nucleus. This assumption is favored by a comparison of Γ_{exp} for the two compounds: the line broadening is greater for $IrSn_2$, where the Ir atom has a larger number of uncompensated spins.

INVESTIGATION OF CHEMICAL SHIFTS IN $IrSn_2-PtSn_2$ SOLID SOLUTIONS

As already stated, the two compounds $IrSn_2$ and $PtSn_2$ have the same crystal structure, so we may assume that in the quasibinary system $IrSn_2-PtSn_2$ a continuous sequence of solid solutions should be formed. To study the Mössbauer effect, we prepared alloys of the quasibinary section $IrSn_2-PtSn_2$ with 25, 50 and 70 mol% $PtSn_2$. The samples were examined with x-rays and it was established that the CaF_2 structure is preserved for the ternary alloys $Ir(Pt)Sn_2$, while the lattice parameter increases linearly from $IrSn_2$ to $PtSn_2$:

Mol% $PtSn_2$:	$IrSn_2$	25	50	75	100
a, Å:	6.34	6.36	6.38	6.41	6.43

All three alloys gave single Mössbauer lines. The results of studies of the chemical shift are given in Fig. 2. The dependence of δ on the mol % of $PtSn_2$ is linear. When there is s-d exchange coupling, some of the conduction electrons, including the 5s-electrons of Sn, can participate in indirect exchange with the d-band electrons. This exchange is greater for Ir, which has a larger number of holes in the d-band. Thus the number of 5s-electrons of Sn participating in s-d exchange with Ir is greater, but as we add Pt the capacity of the d-band decreases and the chemical shift becomes larger.

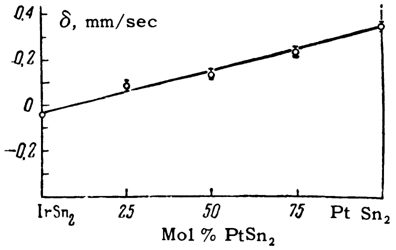

FIG. 2. Dependence of chemical shifts (relative to Mg_2Sn source) for 23.8-keV γ quanta from Sn^{119} on the molecular composition of the quasibinary section $IrSn_2-PtSn_2$.

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