LATTICE DYNAMICAL INVESTIGATION OF MÖSSBAUER RESONANCE STRENGTH AND THERMAL ENERGY SHIFT FOR 23.87 keV GAMMA-RAY OF Sn119 IN IRON LATTICE

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LATTICE DYNAMICAL INVESTIGATION OF MÖSSBAUER RESONANCE STRENGTH AND THERMAL ENERGY SHIFT FOR 23.87 keV GAMMA-RAY OF Sn^{119} IN IRON LATTICE

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Résumé. — Dans le cadre de la théorie de Mannheim de la dynamique d'une impureté de réseau et à l'aide de la fonction de distribution de fréquence des phonons déterminée expérimentaleme nt pour le réseau de la matrice, on analyse les mesures récentes de la fraction Mössbauer et du déplacement d'énergie des rayons γ de 23,87 keV de ^{119}Sn dopant un réseau de fer. La variation de la constante de force (λ'/λ) due à l'impureté donnant un bon lissage de la fraction Mössbauer mesurée est égale à 0,4 en contraste avec la valeur de 1,0 qui a été publiée par Price. En comparant les deux quantités mesurées mentionnées ci-dessus, on déduit un paramètre important—la vitesse quadratique moyenne absolue au point zéro — relié à la température critique du supraconducteur. On évalue également l'énergie cinétique au point zéro de ^{119}Sn dans le fer. On étudie finalement l'effet d'une impureté lourde en comparant ces quantités à celles correspondantes de ^{57}Fe dans le fer.

Abstract. — Recently measured Mössbauer fraction and gamma-ray energy shift for 23.87 keV gamma-ray of Sn^{119} doped in iron lattice are analysed in the framework of Mannheim theory for impurity lattice dynamics and using the experimentally measured phonon frequency distribution function for the host lattice. The force constant change due to impurity, λ'/λ, which gives a good fit to the measured Mössbauer fraction turns out to be 0.4 in contrast to 1.0 reported by Price. By intercomparing the two above-mentioned measured quantities, an important parameter — absolute zero-point mean square velocity — related to the critical temperature of the superconductor is deduced. Zero-point kinetic energy of Sn^{119} in iron is also evaluated. Finally, by comparing these quantities with the corresponding quantities for Fe^{57} in iron, the effect of heavy impurity is studied.

1. **Introduction.** — It is well known that Mössbauer spectroscopy [1] can give direct information on the dynamical properties of the resonant atom if the strength of the resonant absorption and peak displacement are measured as a function of temperature [2]. The first is related to the mean square displacement $< x^2 >$, and the second to the mean square velocity $< v^2 >$, of the resonant atom. Here it may be mentioned that Mössbauer spectroscopy has an advantage over the neutron scattering technique as far as the dynamics of the impurity is concerned. The neutrons are sensitive mainly to the host lattice, the phonon spectrum of which is only very slightly perturbed by the introduction of the impurity, whereas, the Mössbauer effect of the impurity itself is sensitive only to the phonon spectrum of the impurity which can be weighted very differently from that of the host. Since an impurity atom will affect the lattice dynamics of the host, due to change of the mass and change of the coupling constant, the measurement of the above-mentioned quantities on comparing with the theoretical model for the impurity [3-9] can yield the value of the change of the coupling constant due to the presence of the impurity [10-14]. By subtracting the second-order Doppler contribution to the total measured energy shift, one can study the temperature dependence of isomeric shift or s-electron density at the nucleus [14, 15].

Recently, Price [16] has studied the temperature dependence of hyperfine interaction at Sn^{119} nuclei in iron at temperatures between 4.2 and 972 K using Mössbauer spectroscopy. Employing the Debye spectrum for the host lattice, they have shown that the tin ion vibrates as an isotopic impurity in the iron matrix. In view of the availability of the measured phonon spectrum for iron, it was decided to re-estimate the force constant change using the Mannheim expression [9] for $< x^2 >$. Here it may be pointed out that because of the approximations involved in Mannheim's model [9], this can give only a rough estimate of force constant change λ'/λ due to the impurity ; this paper is written under this reservation.

By combining the experimentally measured energy shift $(\delta E(T))$ and Mössbauer fraction $f(T)$ at various temperatures, absolute root mean square zero-point velocity, is deduced [17]. Zero-point motion $(\delta v/c)_{ZP}$ produces a sizeable second-order Doppler shift in the gamma ray energy, e. g., for molecular solids Hazony [18] has shown that this temperature-independent term is comparable to the isomer shifts. The zero-

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point kinetic energy which expresses the internal energy of tin in iron host crystal at 0 K is also derived. An important quantity — ratio of the expectation of the mean square velocity to the mean square displacement within the lattice near zero temperature — which is related to critical temperature in superconductivity [19] is also studied.

Finally, it was decided to compare these with the corresponding quantities for the pure iron lattice so that the effect of heavy impurities on various parameters could be studied.

2. **Theory.** — The probability of the recoilless γ-ray emission, f, from a nucleus bound in a mono-atomic cubic crystal is given by

$$f(T) = \exp(-K^2 < x^2 >_{av}) \tag{1}$$

$< x^2 >_{av}$ is the mean square displacement of the emitting nucleus along the direction of gamma ray emission and $K = 2\pi/\lambda$ is the gamma-ray wave number

The second experimentally measured quantity δE the total central shift of the gamma ray energy, can be written as [17]

$$\frac{\delta E(T)}{E} = \left(\frac{\delta E^{2D}}{E}\right)_a + \left(\frac{\delta E^{2D}}{E}\right)_s + \left(\frac{\delta E^{IS}}{E}\right)_{s-a} \tag{2}$$

where $(\delta E^{IS})_{s-a}$ is the isomer shift (IS) of the source with respect to the absorber and $(\delta E^{2D})_s$ and $(\delta E^{2D})_a$ are the second-order Doppler (SOD) shift of the source and absorber atoms, respectively. The IS of the energy levels of the absorber with respect to the source is a result of the different electrostatic interactions of these nuclei with the field of the surrounding electrons. On the basis of a simple model, the IS in non-relativistic approximation is given by [20]

$$\frac{\delta E^{IS}}{E} = \frac{2\pi}{E} Ze^2(R_e^2 - R_g^2)\left[|\psi_a(0)|^2 - |\psi_s(0)|^2\right] \tag{3}$$

where R_e and R_g are the nuclear radii of the excited and ground states and $|\psi_a(0)|^2$ and $|\psi_s(0)|^2$ are the total s-electron densities at the absorber and emitting nuclei. On the other hand, energy shift due to the SOD effect which can equivalently be considered as arising from the change in the mass of the emitting lattice due to the loss of a photon having a relativistic mass equivalent to E/c^2 is given by [21, 22]

$$\frac{\delta E^{2D}}{E} = -\frac{< v^2 >}{2c^2} \tag{4}$$

where $< v^2 >_{av}$ is the mean square velocity of the resonant nucleus. It is these $< x^2 >$ and $< v^2 >$ which depend on the lattice spectrum and, in terms of this, are given by

$$< x^2 >_{av} = \frac{\hbar}{2M'} \int_0^{\omega_{max}} \omega^{-1} \operatorname{Coth}\left(\frac{\hbar\omega}{2kT}\right) G_I(\omega)\, d\omega$$

$$= \frac{\hbar}{2M'} < \omega^{-1} > \tag{5}$$

$$< v^2 >_{av} = \frac{3\hbar}{2M'} \int_0^{\omega_{max}} \omega \operatorname{Coth}\left(\frac{\hbar\omega}{2kT}\right) G_I(\omega)\, d\omega$$

$$= \frac{3\hbar}{2M'} < \omega^1 > \tag{6}$$

where M' is the mass of the impurity atom and $G_I(\omega)$ is the dynamic response function for the impurity atom. For calculating this we shall make use of the Mannheim theory [9], which employs symmetry properties of the body-centered (and face-centered) cubic lattices and assumes harmonic central forces, limited to nearest neighbour interaction between the impurities and the host. In the absence of the localized or resonance impurity modes, $G_I(\omega)$ is defined as [9]

$$G_I(\omega) = \frac{M}{M'} G_H(\omega) \left\{ [1 + \rho(\omega)\, S(\omega)]^2 + \left[\frac{\pi}{2} \omega G_H(\omega)\, \rho(\omega)\right]^2 \right\}^{-1} \tag{7}$$

$G_H(\omega)$ is the phonon frequency distribution function for the host lattice and

$$\rho(\omega) = \frac{M}{M'} - 1 + \frac{2\omega^2}{\omega_{max}^2}\left(1 - \frac{\lambda}{\lambda'}\right)$$

$$S(\omega) = \int_0^{\omega_{max}} \omega'^2 \frac{G_H(\omega')\, d\omega'}{(\omega'^2 - \omega^2)}. \tag{8}$$

For a given $G_H(\omega)$ and a specified impurity mass the only unknown parameter appearing in the above equation is the force constant ratio λ'/λ and can be adjusted for optimal fit to the experimental data.

Regarding the second aspect of the problem, viz. the estimation of zero-point motion, we shall consider eq. (2). Here it is important to point out that in the experimental study of Price [16] the source. $BaSn^{119}O_3$ was kept at room temperature and was moved relative to the absorber, consisting of approximately 1 wt % tin (enriched to 84 % ^{119}Sn) in iron, which was kept stationary. The temperature of the absorber was varied between 4.2 and 972 K. Thus $(\delta E^{2D})_s$ can be taken as constant independent of the temperature of the absorber. Writing eq. (2) in terms which have more meaning experimentally and separating the zero-point (ZP) velocity and the temperature-dependent contribution to the second-order Doppler term,

$$\frac{\delta E(T)}{E} = \left[\left(\frac{\delta v^{2D}}{c}\right)_T + \left(\frac{\delta v^{2D}}{c}\right)_{ZP}\right]_a + \left[\left(\frac{\delta v^{IS}}{c}\right)_{s-a} + \left(\frac{\delta v^{2D}}{c}\right)_s\right] \tag{9}$$

where δv is the first-order Doppler shift necessary to compensate for the energy shift due to the mechanism indicated by the subscript. Using eq. (1) and (4), eq. (9) can be written as

$$\ln f(T) =$$

$$= \frac{2\,c^2}{\lambda\!\!\!^{-2}} \frac{< x^2 >_{av}}{< v^2 >_{av}} \left\{ \frac{\delta E(T)}{E} - \left[\left(\frac{\delta v^{IS}}{c} \right)_{s-a} + \left(\frac{\delta v^{2D}}{c} \right)_{s} \right] \right\}$$

$$= S(T) \left\{ \frac{\delta E(T)}{E} - \left[\left(\frac{\delta v^{IS}}{c} \right)_{s-a} + \left(\frac{\delta v^{2D}}{c} \right)_{s} \right] \right\} \qquad (10)$$

where

$$S(T) = \frac{2\,c^2}{\lambda\!\!\!^{-2}} \frac{< x^2 >_{av}}{< v^2 >_{av}} = \frac{2\,c^2}{3\,\lambda\!\!\!^{-2}} \frac{< \omega^{-1} >}{< \omega^{1} >}$$

and turns out to be constant (nearly independent) at high temperature. Thus, assuming IS to be temperature independent, the slope of $\ln f(T)$ versus $\delta E(T)/E$ determines $S(\infty)$ at high temperature. Combining the measured $S(\infty)$ with $S(0)/S(\infty)$ calculated from the theoretical model (eq. (5)-(8)) one can calculate $S(0)$ and hence $\left.\frac{< \omega^{-1} >}{< \omega^{1} >}\right|_{ZP}$. Once $S(0)$ is known, then

$$\left(\frac{\delta v^{2D}}{c} \right)_{ZP} = \left(\frac{\delta E^{2D}}{E} \right)_{ZP}$$

can be calculated, from the measured recoil-free fraction $f(0)$, by

$$\left(\frac{\delta v^{2D}}{c} \right)_{ZP} = \frac{\ln f(0)}{S(0)} . \qquad (11)$$

3. **Calculations.** — Using eq. (5), (7) and (8) we have calculated $f(T)$ over a temperature range 4.2-1 000 K for various values of λ'/λ. The calculation was done in the harmonic approximation since it has been shown in our earlier communication that anharmonicity is very small in the case of iron lattice [15, 23]. The phonon spectra for host lattice $G_H(\omega)$ was taken from the work of Minkiewicz *et al.* [24]. Calculated results for $f(T)/f(T = 4.2)$ are plotted in figure 1 along with the experimental measurements of $a(T)/a\,(T = 4.2)$ by Price [16] $a(T)$ represents the area under the resonance absorption curves at temperature T and is assumed to be proportional to the strength of resonance absorption $f(T)$. It is seen clearly that $\lambda'/\lambda = 0.4$ fits the experimental data very well. In fact the discrepancy at low temperature can be removed by incorporating the magnetic effects to the measured phonon frequencies as has been done in our earlier work [23] and is not of much use to include here. Our value of $\lambda'/\lambda = 0.4$ is in contrast with the value 1.0 predicted by Price on the basis of Debye theory.

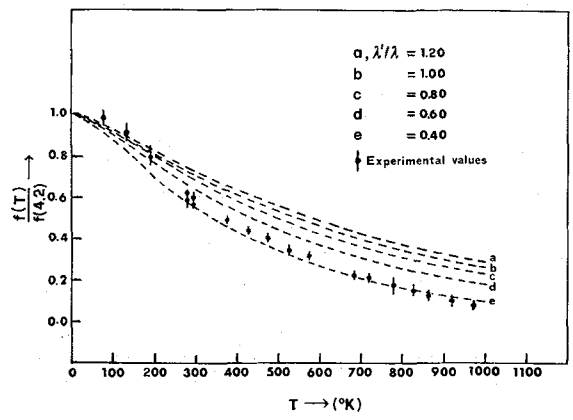

FIG. 1. — Temperature dependent Mössbauer fraction of 23.87 keV γ-rays of ^{119}Sn in iron lattice for different values of λ'/λ along with the experimental values [16].

Figure 2 shows the variation of calculated $\ln f$ versus $((\delta E^{2D})/E)_a$ at various temperatures for $\lambda'/\lambda = 0.4$

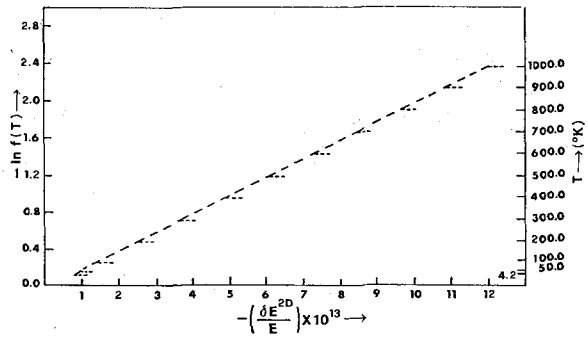

FIG. 2. — Variation of calculated $\ln f(T)$ versus energy shift due to SOD effect $(\delta E^{2D}/E)_a$ at various temperatures.

giving $S(T) = \ln f(T)/(\delta E^{2D}/E)$ to be 0.149 0 and 0.196 3 × 10^{13} at low (T = 4.2 K) and high temperatures giving $S(0)/S(\infty) = 0.759\,0$. Figure 3 shows a similar curve, but from the experimentally measured quantities. The measured energy shifts at constant

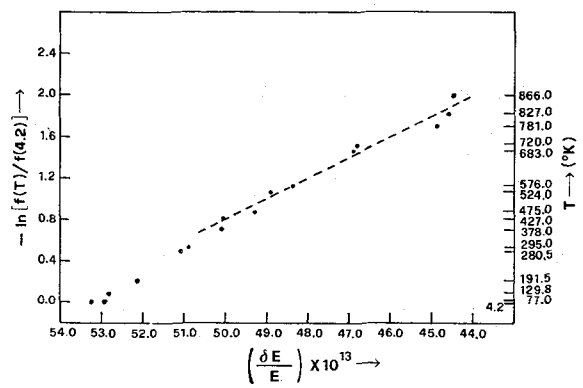

FIG. 3. — Variation of measured $\ln [f(T)/f(4.2)]$ versus total energy shift $(\delta E/E)$ at various temperatures [16].

pressure were converted to constant volume through the standard thermodynamic relation (eq. (13), ref. [16]). Here we have plotted the relative values of $f(T)$ as these are the only values available and, in fact, it has been shown [17] that it is not even necessary to know the absolute measurements of $f(T)$ in order to determine $S(\infty)$. The dotted line through the experimental points is the least square fit according to

eq. (10). The slope of this line, which gives $S(\infty)$, turns out to be $0.199\,8 \times 10^{13}$, and the intercept

$$-S(\infty)\left[\left(\frac{\delta v^{IS}}{c}\right)_{s-a}+\left(\frac{\delta v^{2D}}{c}\right)_{s\text{ at RT}}\right]=-10.794\,4$$

or

$$\left(\frac{\delta v^{IS}}{c}\right)_{s-a}+\left(\frac{\delta v^{2D}}{c}\right)_{s\text{ at RT}}=54.026\times10^{-13}$$

giving $(\delta v^{IS})_{s-a}+(\delta v^{2D})_{s\text{ at RT}}=1.620\,8$ mm/s.

Thus if the energy shift due to SOD effect for the Sn atom in $BaSnO_3$ (source) at room temperature is calculated separately, the change in the IS (hence s-electron density) between source and absorber can easily be calculated.

Now combining the obtained $S(\infty)$ with $S(0)/S(\infty)$ obtained theoretically, one has

$$S(0)=\frac{\ln f(0)}{\left(\frac{\delta v^{2D}}{c}\right)_{ZP}}=0.151\,6\times10^{13}$$

$$=\frac{2c^2}{3\lambda^2}\left[\frac{<\omega^{-1}>}{<\omega^{1}>}\right]_{ZP}$$

giving

$$\left[\frac{<\omega^{-1}>}{<\omega^{1}>}\right]_{ZP}=0.001\,7\times10^{-24}\qquad(12)$$

and

$$\left.\frac{\delta v}{c}\right|_{ZP}=-\frac{<v_0^2>_{av}}{2c^2}=\frac{\ln f(0)}{S(0)}=-\frac{0.119\,0}{0.151\,6\times10^{13}}$$

$$=-0.784\,7\times10^{-13}\qquad(13)$$

$<v_0^2>$, mean square velocity of the resonant atom at 0 K

$$=-2c^2\left(\frac{\delta v}{c}\right)_{ZP}=14.124\,6\times10^{7}\ \mathrm{cm^2/s^2},$$

zero-point velocity

$$v_{ZP}=<v_0^2>^{1/2}=1.188\,5\times10^{4}\ \mathrm{cm/s},\qquad(14)$$

and zero-point displacement

$$x_{ZP}=<x_0^2>^{1/2}=\lambda[-\ln f(0)]^{1/2}$$

$$=0.028\,4\times10^{-8}\ \mathrm{cm}.\qquad(15)$$

Finally, zero-point kinetic energy of Sn^{119} in iron lattice

$$=\tfrac{1}{2}M'<v_0^2>=0.008\,78\ \mathrm{eV}.\qquad(16)$$

4. Discussion and conclusions. — Firstly, we have shown that for Sn^{119} in iron, the force constant change λ'/λ is 0.4, which suggests weak binding for the impurity, i. e. the Sn atom in iron lattice is weakly bound in comparison with the iron atom itself. Secondly, we have calculated various dynamical properties by combining resonance strength and energy shift at various temperatures. To make some qualitative remarks regarding the effect of heavy impurity we compare the corresponding quantities for ^{57}Fe doped in iron lattice [17]. The results are summarized in table I. The important quantity which we should like to compare is the effect of heavy impurity on

$$[<\omega^{1}>/<\omega^{-1}>]_{ZP},$$

as from the result of McMillan's work [19] the decrease in this quantity corresponds to an increase in the critical temperature of the superconductor (although the detailed understanding of the superconductivity would depend upon the superconducting coherence length and upon the physical extent of the parameter $[<\omega^{1}>/<\omega^{-1}>]_{ZP}$ associated with the heavy impurity). We find from the table that this is decreased by the addition of heavy impurity and

$$[<\omega^{1}>/<\omega^{-1}>]_{ZP}^{Sn-Fe}/[<\omega^{1}>/<\omega^{-1}>]_{ZP}^{Fe-Fe}$$

is 0.415 2.

TABLE I

Parameter	Sn^{119} in iron	Fe^{57} in iron [17]
—	—	—
1. Experimental $S(\infty)\times10^{-13}$	0.199 8	0.032 8
2. Theoretical $\frac{S(0)}{S(\infty)}$	0.759 0	0.699 0
3. $\left.\frac{<\omega^{1}>}{<\omega^{-1}>}\right\|_{ZP}\times10^{-24}$	584.795 3	1 408.450 7
4. $\left(\frac{\delta v^{2D}}{c}\right)_{ZP}\times10^{13}$	0.784 7	3.76
5. $v_{ZP}\times10^{-4}$, cm/s	1.188 5	2.60
6. $x_{ZP}\times10^{8}$, cm	0.028 4	0.039 3
7. ZP kinetic energy, eV	0.008 78	0.020 12

Finally we shall calculate the increase in the internal energy at 0 K, which results from the alloying of tin atoms to iron lattice and is given by the difference of the zero-point kinetic energy between iron and solute tin atoms. From the last row of table I this turns out to be 0.011 34 eV.

A similar calculation of the systems ^{57}Fe in gold and

^{197}Au in gold can be made to study the effect of light impurity.

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