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Anomalous temperature dynamics of impurities in metals: A kinetic model

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A kinetic model for the dynamical behavior of strongly fluctuating impurity atoms (IA's) in nanometer environment in metals is suggested. The model describes large, reversible picosecond displacements of IA's which can cause experimentally observable "anomalous" effects. The model is based on the kinetic many-body electron-related theory of short-lived large energy fluctuations (SLEF's) of atomic particles of the peak-thermal energy $\varepsilon_{\rm op} \geq \Delta E \gg kT$ and lifetime $\Delta\tau = 10^{-13}-10^{-12}$ s. (ΔE is the threshold energy of reversible SLEF's, sufficient to produce large transient reversible IA displacements which are not accompanied by IA hopping over energy barriers ΔE_d since $\Delta E < \Delta E_d$.) SLEF-induced dynamics of picosecond, atomic and electronic phenomena in the nanometer IA vicinity correlated with the IA motion is considered. The model is applied to the dynamics of Sn impurities in Pb-Sn, Ag-Sn, and Au-Sn alloys with small Sn concentrations. Measurable parameters for these alloys are calculated, and an agreement with published experimental data in Mössbauer spectroscopy is found.

I. INTRODUCTION

During the last decade experiments showing anomalous temperature behavior of impurity metal atoms have been reported for a few host metals.[1-4] The anomalous temperature behavior of impurity atoms was first observed through x-ray-absorption fine-structure (XAFS) measurements on Hg impurities in Pb host lattice.[3] Then Mössbauer experiments following the XAFS studies have also given evidence of the anomalous dynamic behavior of similar systems.[1,2] It has been observed that ^{119}Sn atoms in metals (e.g., in Pb, Ag, and Au) display an abnormal temperature dependence of the Mössbauer spectral intensity (MSI) when a certain temperature T_0 (substantially lower than the host melting point T_M) is approached. These studies show that when T approaches $T_0 < T_M$ the MSI falls below the expected Debye-Waller line related to the ordinary thermal behavior[1-4] described by the Debye-Waller factor (DWF)

$$f_M^{(0)} = \exp(-Q_\gamma^2 \sigma_A^2) \ . \tag{1.1}$$

Here $Q_\gamma = \lambda_\gamma^{-1}$ is the γ wave number, σ_A^2 is the mean-square displacement of the impurity atoms (IA's). The observed temperatures T_0 are too low to be associated with diffusion of the IA's with reasonable rates. For instance, T_0 (Sn in Pb)$\approx 0.25 T_M$(Pb), and T_0(Sn in Ag)$\approx 0.7 T_M$(Ag), where T_M(Pb)≈ 600 K and T_M(Ag) ≈ 1234 K.

Above T_0, the MSI exhibits a substantially increased rate of the dropoff with a rise in temperature, but no line broadening is observed. This rapid MSI dropoff cannot be explained by the ordinary anharmonic atomic motion. The observed steepness in the MSI dropoff looks as if the IA's experience large displacements $\Delta q_0 = |q_0 - \bar{q}_0| > \lambda_\gamma$ due to the thermally activated motion with frequencies

$$K = K_0 \exp(-\Delta E / kT) \ , \tag{1.2}$$

where $\Delta E \gg kT$ is the activation energy. However, this activated IA motion cannot be attributed to long-range diffusion since T_0 is too low to yield a reasonable K if ΔE is related to atomic diffusion. It is possible that the observed anomalies in the MSI are related to some qualitatively new local generic dynamical fluctuational phenomena around the IA which start to be significant at $T \approx T_0$, but which have not been considered in the conventional theory of the Mössbauer effect.[5,6] The explanation of the observed anomalous temperature MSI behavior, probably, requires invoking new ideas related to the motion of IA's and dynamical instabilities in the IA neighborhood, which are induced by short-lived large energy fluctuations of the IA's and their neighbors.

A phenomenological model which assumes an anomalously rapid hopping of the IA between local potential wells around the IA lattice site has been proposed.[1-4] In this model the hopping of the IA takes place within a "bubble" containing a large entropy density and involving a coherent motion of some 20–40 surrounding atoms. The model assumes that local potential in the IA vicinity forms potential wells separated by barriers U_h substantially large than kT_0 but smaller than the energy barriers ΔE_d overcome in atomic diffusion. In addition, local disordering is assumed to occur in the IA vicinity that promotes the rapid hopping of the IA between the local potential wells that, in turn, causes the observed anomalies in the MSI. This mechanism shows that the observed MSI anomalies can be associated with transient many-body phenomena occurring in the nanometer IA vicinity. Using certain phenomenological fitting parameters, a reasonable agreement with experimental data is obtained.[1-4] The dynamics of the involved many-body phenomena was not considered in the phenomenological model.[1-4]

In this paper we propose a new dynamical many-body approach to the anomalous thermal motion of IA's which considers picosecond atomic and electronic processes in the IA nanometer vicinity correlated with the "anomalous" IA motion. This approach results in some experi-

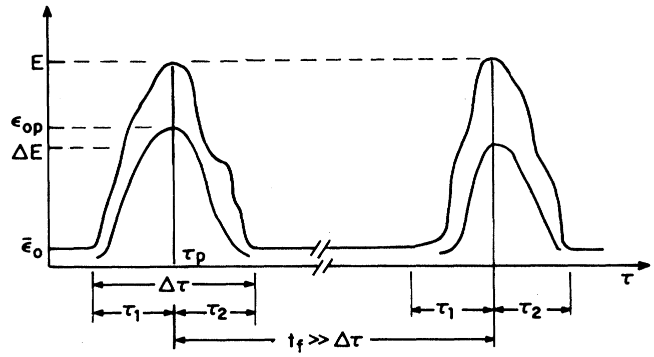

FIG. 1. Time and energy scales of the two successive SLEF's of a single atom (or of $N_0 \geq 1$ atoms) up to peak thermal energy $\varepsilon_{\mathrm{op}} \geq \Delta E >> kT$. ΔE is the SLEF threshold energy sufficient to produce large transient reversible displacements $\Delta q_0 > \lambda_\gamma$ of the impurity atoms able to destroy the Mössbauer effect. $\Delta\tau = 10^{-13}$–10^{-12} s is the SLEF lifetime, $\tau_1 \approx \Delta\tau/2$ is the SLEF formation time, $\tau_2 \approx \tau_1$ is the SLEF relaxation time. $t_f \approx W^{-1} >> \Delta\tau$ is the average time between the two successive SLEF's of $\varepsilon_{\mathrm{op}} \geq \Delta E$ affecting the same atoms, W is the SLEF probability per second, $\bar{\varepsilon}_{\mathrm{op}}$ is the mean thermal energy of the N_0 atoms.

mentally observable effects reported recently[1–4] and the model shows substantial deviations from the usual IA thermal behavior in solids. Our model considers these anomalies in the IA thermal motion to be a generic consequence of reversible short-lived large-energy fluctuations (SLEF's) of single atoms (or of small clusters of $N_0 \geq 1$ atoms) up to the peak thermal energy $\varepsilon_{\mathrm{op}} >> kT$, which have lifetime $\Delta\tau = 10^{-13}$–10^{-12} s (Figs. 1 and 2). These SLEF's generate reversible large transient atomic displacements (LTAD's) Δq_0 much larger than the average atomic displacements σ_A (Fig. 3). The reversible SLEF's supply the IA's with the thermal energy $\varepsilon_{\mathrm{op}}$ sufficient to cause the reversible LTAD's (Fig. 3) but insufficient for IA diffusion jumps over energy barriers (Fig. 2). The dynamics of irreversible and reversible SLEF's and LTAD's of hyperthermal fluctuating particles (HFP's) and the accompanying motion of atoms and electrons in the HFP nanometer vicinity, which were described in our previous work[7–15] are manifested themselves in molecular-dynamics simulations.[12,13]

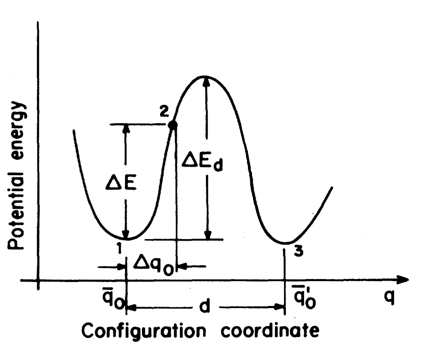

FIG. 2. Diagram of the two neighboring potential wells separated by the barrier of height ΔE_d larger than the SLEF threshold energy $\Delta E < \Delta E_d$ sufficient to generate large displacements $\Delta q_0 > \lambda_\gamma$ of the impurity atom (position 2). This atom excited by a reversible SLEF does not overcome the energy barrier ΔE_d and cannot come to position 3.

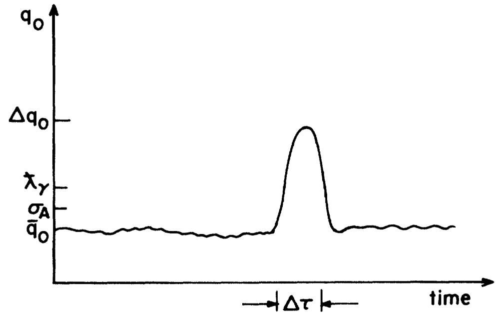

FIG. 3. A large SLEF-induced reversible displacement $\Delta q_0 |q_0 - \bar{q}_0| > \lambda_\gamma$ of an impurity atom (of coordinate q_0) from its mean position of coordinate $\bar{q}_0$.

We apply the reversible SLEF's and LTAD's to propose a new dynamical many-body electron-related model that suggests an explanation for the observed MSI anomalies in terms of the local SLEF-induced picosecond "violent" correlated motion of the IA's and their nanometer surroundings. In our model, the picosecond reversible violent motion of the IA's, the formation of a local transient nanometer "bubble" and disordering in the IA vicinity are generated by SLEF's of single atoms (or of small clusters of $N_0 \geq 1$ atoms). The HFP's acquire large picosecond reversible deviations $\Delta q_0 = |q_0 - \bar{q}_0| > \lambda_\gamma$ of their coordinates q_0 from the mean values $\bar{q}_0$ without jumping over energy barriers. A single SLEF affects the nanometer HFP vicinity containing a few tens of atoms and produces local disordering in this region.[7–15] This is, in a sense, similar to those of the local "bubble" introduced in the bubble model.[1–4]

In our model it is not necessary to assume the existence of local potential wells in the IA vicinity or IA's hopping between the wells. The IA's affected by the SLEF's can move in a region of a linear dimension $\Delta q_0 > \lambda_\gamma$. Thus the region from which the IA emits the γ-wave train is larger than λ_γ. Therefore, pieces of the γ-wave train emitted by the SLEF-affected IA's from different points of the region of the radius larger than λ_γ may interfere destructively. Consequently, one can observe the rapid decrease in the recoilless fraction f_M of γ emission around a certain temperature T_0 at which the SLEF-induced phenomena become essential. In this way, the SLEF-driven IA's cause the observed rapid dropoff in the MSI. We show in the following sections that the SLEF probability for SLEF's of $\varepsilon_{\mathrm{op}} \geq \Delta E >> kT$ become large enough to produce the observed rapid dropoff in the MSI. Here ΔE is the SLEF threshold energy sufficient to induce the observed anomalies in the MSI. ΔE appears substantially smaller than the diffusion activation energy ΔE_d. This explains why the MSI anomalies are observed at low temperatures considerably lower than T_M.

The paper is organized as follows. The Introduction is followed by the statement of the problem (Sec. II). A dynamic model of large picosecond reversible atomic energy and coordinate fluctuations in nanometer regions of solids is described in Sec. III. The destructive influence of reversible atomic SLEF's on the Mössbauer effect is discussed in Sec. IV. The critical temperature T_0 for the rapid decrease in the recoilless Mössbauer fraction is calculated in Sec. V. Discussion and comparison of theoretical calculations with the observed anomalous temperature behavior in Mössbauer experiments are given in Sec. VI. A summary is presented in Sec. VII.

II. STATEMENT OF THE PROBLEM

The anomalies in the temperature MSI behavior are observed at temperatures $T=T_0$ considerably lower than the melting point T_M, but nevertheless sufficiently high (higher than the Debye temperature Θ), and therefore, quantum effects in the atomic motion can be neglected. That is why the semiclassical approximation model is used, where the atomic motion is described classically while electrons are treated quantum mechanically.

The conventional theory of the atomic motion in solids applied to the Mössbauer effect involves the following two main types of the atomic motion: the atoms of the first type perform harmonic oscillations about their lattice sites with small mean-square deviations $\sigma_A < \lambdabar_\gamma$ from their equilibrium position.[5,6] The harmonic regime can be perturbed by relatively small anharmonic vibrations. This mechanism leads to the regular decrease in the MSI with temperature described by DWF (1.1). The second type of the atomic motion is associated with atomic diffusion. The simple physical interpretation of the standard DWF (Ref. 5) states: "The continuously emitted electromagnetic wave comes from a region of linear dimension $\langle x^2\rangle^{1/2}$ (in our notation $\langle x^2\rangle=\sigma_A^2$). If the linear dimension of the region from which the γ emission occurs increases beyond the wavelength $\lambdabar_\gamma$, pieces of the wave train emitted from different points in this region interfere destructively. In this case the fraction f_M of photons emitted without a loss decreases rapidly." The SLEF theory predicts[7-11] (and molecular-dynamics simulations[12,13] confirm) that SLEF's can cause violent reversible LTAD's $\Delta q_0=|q_0-\bar{q}_0|>\lambdabar_\gamma$ of the atoms involved. If this happens with γ-emitting IA's, the condition for the recoilless γ emission

$$\sigma_A Q_\gamma < 1$$

or (2.1)

$$\sigma_A < 0.1\ \text{Å} \approx (3\text{–}5)\times 10^{-2}\, d$$

is broken and the recoilless fraction falls. Here $d=(2-3)$ Å is the mean interatomic distance. For instance, for ^{119}Sn, $Q_\gamma=\lambdabar_\gamma^{-1}=12.1$ Å^{-1}, whereas SLEF-induced LTAD's Δq_0 can be much larger than 0.1 Å.

Thermally activated atomic diffusion characterized by the diffusion coefficient

$$D=D_0\exp(-\Delta E_d/kT) \tag{2.2}$$

can cause, mainly, a line broadening of $\Gamma_d \cong \hbar D/\lambdabar_\gamma^2$. However, the observed rapid MSI dropoff occurs at temperatures $T=T_0=(0.25-0.7)T_M$ which are too low for atomic diffusion to produce a discernable effect on the MSI. Thus at $T=T_0$ effects of atomic diffusion can be neglected. For instance, for Sn diffusion in Pb, at $T=T_0=150$ K, the following parameters hold:

$$\begin{aligned}&\Delta E_d(\text{Sn}\rightarrow\text{Pb})=1.1\ \text{eV}\ ,\\ &D_0=2\ \text{cm}^2/\text{s}\ ,\\ &D=5\times10^{-37}\ \text{cm}^2/\text{s}\ ,\\ &K=\frac{6D}{\rho^2}=3\times10^{-21}\ \text{s}^{-1}\ ,\end{aligned} \tag{2.3}$$

and

$$n_d=t_M K=3\times10^{-28}\ .$$

Here K is the frequency of diffusion jumps per atom, n_d is the number per Sn atoms of diffusion jumps during the Mössbauer characteristic time $t_M=\hbar/\Gamma_M\approx10^{-7}$ s, where Γ_M is the natural width.

This situation has motivated the authors[1-4] to propose a model which assumes the existence of local potential wells in the immediate surroundings of the IA's which are separated by barriers of height U_h substantially lower than diffusion barriers ΔE_d. Under these circumstances the IA's can execute fast hopping between the local potential wells around particular lattice sites at low temperature. This phenomenological model does not consider the dynamics of the local processes involved in the violent IA's motion and in local disordering which causes the formation of the high entropy "bubble" of 20–40 particles. In the SLEF-based model presented here we consider the fourth type of the atomic motion in the solid, associated with the permanent presence in the crystal of HFP's generated by a reversible SLEF of the peak thermal energy $\varepsilon_{\text{op}}\gg kT$, which satisfies the condition $\varepsilon_{\text{op}}<\Delta E_d$ (Fig. 2).[7(a),12-15] The reversible SLEF's which do not produce atomic diffusion are able to initiate LTAD's Δq_0 and large velocity fluctuations Δv_{op} which satisfy the following conditions (Figs. 2 and 3):

$$\Delta q_0=|q_0-\bar{q}_0|>\lambdabar_\gamma=Q_\gamma^{-1}$$

and (2.4)

$$\Delta v_{\text{op}}\gg\bar{v}_0\approx(kT/M)^{1/2}\ .$$

Here $\Delta v_{\text{op}}=v_{\text{op}}-\bar{v}_0$ and $v_{\text{op}}=(\varepsilon_{\text{op}}/M)^{1/2}\gg\bar{v}_0$ is the HFP maximum velocity related to the HFP of peak thermal energy ε_{op}, mass M, and $\bar{v}_0\approx(kT/M)^{1/2}$.

The idea about the possibility of large local nonequilibrium fluctuations in the equilibrium system was suggested by Boltzmann.[16] Later Frenkel[17] was the first to stress the many-body character of the large fluctuations in solids and to point out serious difficulties in the consideration of the related many-body problems. The kinetic many-body theory of SLEF's of a small number $N_0\geq1$ of particles in dense matter and its applications[7-15] is an attempt to implement Boltzmann's[16] and Frenkel's[17] ideas through the dynamic description of a SLEF-induced correlated picosecond motion of the N_0 HFP's and their nanometer surroundings.[7,18] Recently,[19] SLEF-induced local picosecond phenomena in nanometer regions of solids have been considered in terms of local heterophase fluctuations and phase transitions, and agreement with other related results was found.

III. DYNAMICAL MODEL OF LARGE PICOSECOND ATOMIC ENERGY AND COORDINATE FLUCTUATIONS IN NANOMETER REGIONS OF SOLIDS

The theory of SLEF's and SLEF-related phenomena is well documented in the literature.[7–15] Here we summarize, mainly, some key points of this theory related to reversible SLEF's and SLEF-induced LTAD's given by Eq. (2.4), which take the central role in the phenomena discussed in this paper. The SLEF lifetime $\Delta\tau=\tau_1+\tau_2=10^{-13}-10^{-12}$ s includes (Fig. 1) (Refs. 7, 12, and 13) the SLEF formation time τ_1, and SLEF relaxation time τ_2. During τ_1, the HFP receives the thermal energy $\varepsilon_{\rm op} \gg kT$ only from its immediate nanometer vicinity of volume $\Omega_1 \approx 4R_1^3$ of radius $R_1=\rho_0+l \approx 10^{-7}$ cm. This volume contains $\Delta N_1=\Omega_1/\Omega_0 \gg 1$ atoms, typically in the range of 20–100 for different particular solids and energies $\varepsilon_{\rm op}$, ρ_0 is the radius of the volume $V_0=(4\pi/3)\rho_0^3$ occupied by the HFP, and Ω_0 is the average volume per atom. The value $l=c_s\tau_1$ is the maximum distance from which the thermal energy can be delivered to the HFP during τ_1; c_s is the energy-transfer velocity in the atomic system (which is of the order of the sound velocity). Hence one concludes that only the $N_1=1+\Delta N_1$ atoms located in the volume $V_1=V_0+\Omega_1\approx\Omega_1 \gg V_0$ can participate directly in SLEF formation due to the causality conditions.[7–15] During the SLEF relaxation time τ_2 the HFP gives the "borrowed" energy back to the surrounding atoms located in its vicinity Ω_1.

Thus during τ_1, a single SLEF (and LTAD) affects the nanometer polyatomic cluster consisting of a few tens of particles which can play the role of the "small bubble" around impurity atoms suggested in Refs. 1–4. The SLEF's and LTAD's of the involved atoms create strong local transient lattice distortions forming transient point defects of lifetime $\approx\Delta\tau$.[7–15] This local disordering caused by a single SLEF should be associated with a large local entropy similar to that attributed to the local bubble introduced in Refs. 1–4. The SLEF-induced local picosecond disordering in the nanometer regions of solids can be described as "local melting."[7(a),10(a),10(b),15] These phenomena can also be considered in terms of local heterophase fluctuations and phase transitions.[19] The SLEF probability $W(\varepsilon_{\rm op},T)$ per unit time is calculated from a solution of the SLEF kinetic equations and has the Boltzmann-like form[7(a),7(b),18]

$$W(\varepsilon_{\rm op}\geq\Delta E,T)=W_0\exp(-\Delta E/kT)\ , \tag{3.1}$$

where the preexponential factor $W_0=\Delta\tau^{-1}\exp(\Delta S_{\rm op}/k)$ includes the change $\Delta S_{\rm op}$ in the local entropy caused by the SLEF.

The N_1 atoms involved directly in SLEF formation are affected by random fluctuational heatings (coolings)[7(a),7(c),8,10(a),10(b),15(b)]

$$\Delta T_1(t)=T_1(t)-T\approx\pm\frac{T}{N_1^{1/2}}\ . \tag{3.2}$$

Here $T_1(t)=T+\Delta T_1(t)$ is the random time-dependent effective temperature of N_1 atoms. For typical numbers $N_1=20-100$ the fluctuations are equal to $\Delta T_1=(0.1-0.2)T$; Eq. (3.2) shows that the N_1 atoms located in volumes V_1 can be overheated by fluctuations up to T_0 (and even higher) if the temperature of the system T satisfies the condition[7(a),8,10(b),15(b)]

$$T_0-T=\delta T<\frac{T}{N_1^{1/2}}\approx(0.1-0.2)T\ . \tag{3.3}$$

This means that one can expect the MSI to decrease rapidly within the temperature interval δT, e.g., $\delta T\approx(15-30)$ K for ^{119}Sn in Pb; here $T_0=150$ K is known from experimental data[3,4] and will be calculated later. The conclusion about the rapid decrease in the MSI within a finite-temperature interval $\delta T \ll T$ near T_0 is in agreement with experimental data.[1–4]

The probability (per unit time) for the SLEF-induced "violent" motion of the IA's is

$$\begin{aligned}P(\varepsilon_{\rm op},T)&\cong(\kappa+1)W(\varepsilon_{\rm op},T)\\&=(\kappa+1)\Delta\tau^{-1}\exp\left[\frac{-\Delta G_{\rm op}}{kT}\right]\end{aligned} \tag{3.4}$$

since each of the IA's is also disturbed by SLEF's of the κ nearest neighbors. Here $\Delta G_{\rm op}=\Delta E-T\Delta S_{\rm op}$ is the activation free energy.

So far we have discussed only atomic phenomena induced by SLEF's in the HFP vicinity. Now we consider the influence of the local picosecond electronic processes initiated by SLEF's in the HFP nanometer vicinity simultaneously with the LTAD's of IA's. The LTAD's are associated with transient point defects of lifetime $\Delta\tau$.[7–15] The valence electrons in the HFP vicinity follow the relatively slow motion of the involved atoms initiated by SLEF's. The quantum-mechanical aspects of such large local picosecond electron distortions and rearrangements initiated by the large atomic displacements are discussed in more detail in Ref. 10(b). The SLEF-induced electronic rearrangements are associated with Δn^d downward or/and $\Delta n^{\rm up}$ upward electron transitions between energy levels separated by average energy distance $\langle\delta e\rangle$.[7–11,14] These transitions occurring in the nanometer HFP vicinity are synchronized with the SLEF's and LTAD's.

The local electron transitions cause the local energy release $\delta E<0$ (or consumption $\delta E>0$) and the corresponding negative (or positive) changes δS in the local entropy in the HFP nanometer vicinity

$$\delta E=-(\Delta n^d-\Delta n^{\rm up})|\langle\delta e\rangle|\ , \tag{3.5}$$

$$\delta S=-(\Delta n^d-\Delta n^{\rm up})k\ . \tag{3.6}$$

Then the electron affected activation energy $\Delta E_{\rm ef}$, entropy $\Delta S_{\rm ef}$, and SLEF probability are[7–11]

$$\Delta E_{\text{ef}} = \Delta E + \delta E, \quad \Delta S_{\text{ef}} = \Delta S_{\text{op}} + \delta S \ , \tag{3.7}$$

and

$$W = \Delta\tau^{-1} \exp(-\Delta G_{\text{ef}}/kT) \ , \tag{3.8}$$

where $\Delta G_{\text{ef}} = \Delta E_{\text{ef}} - T\Delta S_{\text{ef}}$. Hence, one finds the probability (per second) of LTAD's of the IA's

$$P_{\text{ef}}(\Delta E_{\text{ef}}, T) = (x+1)\Delta\tau^{-1}\exp(-\Delta G_{\text{ef}}/kT) \ . \tag{3.9}$$

The fraction of the total time (per IA) occupied by the LTAD's is

$$\beta_g(\Delta E_{\text{ef}}, T) = (x+1)\exp(-\Delta G_{\text{ef}}/kT) \ . \tag{3.10}$$

IV. DESTRUCTIVE INFLUENCE OF REVERSIBLE ATOMIC SLEF'S ON THE MÖSSBAUER EFFECT

During $\Delta\tau$ the moving IA emits the wave train which contains as many as $\omega_\gamma \Delta\tau / 2\pi$ wavelengths; e.g., $\omega_\gamma \Delta\tau/2\pi = 10^6$ for $Q_\gamma = 12.1$ Å^{-1} and $\Delta\tau = 3\times 10^{-13}$ s. The SLEF's generate the LTAD's of emitting nuclei which satisfy condition (2.4). Therefore, a continuously emitted electromagnetic wave comes from the regions of linear dimensions $\Delta q_0 > \lambda_\gamma$. In this case, pieces of the wave train emitted from different points of this region interfere destructively, and consequently the recoilless fraction f_M decreases rapidly.[6] This can be seen in the following two ways. First, one can use the standard equation for the DWF $f_M = \exp[-(\Delta q_0)^2/\lambda_\gamma^2]$ similar to Eq. (1.1) where the small $\sigma_A < \lambda_\gamma$ is replaced with the large SLEF-induced LTAD Δq_0. In this case $\Delta q_0^2/\lambda_\gamma^2 \gg 1$ and f_M becomes very small. The second way is to consider directly the moving emitting nucleus which can be treated classically as a source of waves of frequency ω_γ and damping factor α_γ and which is affected by a phase modulation caused by the SLEF-induced nucleus motion. Accordingly, one finds the standard relation for the electrical field of the emitted wave

$$E_\gamma(t) \approx \exp\left[-i\omega_\gamma t - \frac{\alpha_\gamma t}{2} + iQ_\gamma \Delta\tilde{q}_0(t) \right] \ . \tag{4.1}$$

It is well known that Eq. (4.1) leads to Eq. (1.1) and therefore to the Mössbauer effect when atomic displacements $\Delta\tilde{q}_0(t)$ are small and, consequently, the factor

$$f_M = \lim_{\Delta t \to \infty} \left| \frac{1}{\Delta t} \int_0^{\Delta t} \exp[iQ_\gamma \Delta\tilde{q}_0(\Delta t)] d\Delta t \right|^2 \tag{4.2}$$

is not too small. Here Δt is the total time, e.g., Δt is the time of experimental run (hours or days). In Eq. (4.2), the value $\Delta\tilde{q}_0(\Delta t)$ reflects the following two regimes of the IA motion: (a) small atomic displacements leading to the DWF (1.1) and (b) large SLEF-induced LTAD's $\Delta q_0 > \lambda_\gamma$ which we consider here. In order to separate these two kinds of IA displacements from each other and calculate the effects of SLEF's on f_M we divide the total time Δt into $b = \Delta t/\Delta\tau$ time intervals of duration $\Delta\tau = 10^{-13}$–10^{-12} s of the SLEF lifetime. Therefore one finds from Eq. (4.2)

$$f_M = \left| \lim_{b\to\infty} \frac{1}{b} \sum_{k=1}^{b} \int_{-\Delta\tau^{(k)}/2}^{\Delta\tau^{(k)}/2} d(\Delta t) \exp[iQ_\gamma \Delta\tilde{q}_0(\Delta t)] \right|^2 . \tag{4.3}$$

Here the values

$$\tilde{f}^{(k)} = \left| \frac{1}{\Delta\tau} \int_{\Delta\tau^{(k)}/2}^{\Delta\tau^{(k)/2}} d(\Delta t) \exp[iQ_\gamma \Delta\tilde{q}_0(\Delta t)] \right|^2 \tag{4.4}$$

describe the effect of the thermal motion of the radiating nuclei on the recoilless emission during every individual time interval $\Delta\tau$. According to Eq. (3.10) the fraction $\beta_f(\Delta E_{\text{ef}}, T)$ of the time intervals $\Delta\tau$ is occupied by the SLEF-induced LTAD's $\Delta q_0 > \lambda_\gamma$. For these time intervals the values $\tilde{f}^{(k)} = f^{(k)}$ are very small and, therefore, the recoilless fraction is very low. So, the SLEF-affected violent motion of the emitting nuclei reduces the MSI by the value

$$\Delta f_M(\Delta E_{\text{ef}}, T) \approx (\kappa+1) f_M^{(0)} \exp\left[-\frac{\Delta G_{\text{ef}}}{kT} \right] . \tag{4.5}$$

Here $f_M^{(0)}$ is the conventional DWF (1.1). Thus the temperature behavior of the MSI perturbed by both the SLEF's and the conventional thermal atomic motion is $F_M \approx (1-\beta_f) f_M^{(0)}$ or

$$F_M(\Delta E_{\text{ef}}, T) \approx \left[1 - (\kappa+1)\exp\left[-\frac{\Delta G_{\text{ef}}}{kT} \right] \right] \times \exp(-Q_\gamma^2 \sigma_A^2) \ . \tag{4.6}$$

Equations (4.5) and (4.6) give the lower limit of the SLEF-induced reductions Δf_M of the MSI, since the calculated SLEF-induced dropoff in MSI takes into account only effects of SLEF's of peak energies $\varepsilon_{\text{op}} \geq \Delta E_{\text{ef}}$. The reduction in the MSI caused by other SLEF's of peak energies $\varepsilon_{\text{op}}^{(L)}$ lower than ΔE_{ef} but considerably larger than kT is not taken into account. However, these SLEF's of peak energy $\varepsilon_{\text{op}}^{(L)}$ can also generate a nonlinear violent motion of IA and IA neighbors but of lower intensity. Thus the SLEF's of peak energies $\varepsilon_{\text{op}}^{(L)} < \Delta E_{\text{ef}}$ can also reduce the MSI. As a result, one expects that the measured MSI is $F_M^{(\text{obs})}(T) < F_M(\Delta E_{\text{ef}}, T)$. The effect of SLEF's of $\varepsilon_{\text{op}}^{(L)} < \Delta E_{\text{ef}}$ on the MSI requires a special consideration.

V. CRITICAL TEMPERATURE FOR THE RAPID DECREASE IN THE RECOILLESS FRACTION

Experiments[1–4] show that the MSI decreases rapidly within a relatively narrow temperature interval $\delta T \ll T_0$ near a certain temperature T_0. Such a behavior of the MSI is typical of that observed in phase transitions. In general, a sharp change in measured characteristics of the system considered (in the MSI) caused by a small change δT of the controlled parameter (temperature) can be treated as some kind of a phase transition which occurs within a narrow temperature range δT near T_0. Hence, one can expect that the reversible SLEF's of the peak energy $\varepsilon_{\rm op} \geq \Delta E_{\rm ef}$ which are able to reduce substantially the MSI within δT, should acquire some specific properties around T_0. This expectation is fulfilled, since the cubic density of simultaneously occurring SLEF's of $\varepsilon_{\rm op} \geq \Delta E_{\rm ef}$ at $T \rightarrow T_0$

$$\eta_f(\Delta E_{\rm ef}, T) = d^{-3} \exp\left[-\frac{\Delta G_{\rm ef}}{kT}\right] \tag{5.1}$$

becomes so high that SLEF's initiate a specific dynamic percolationlike process observed as a phase transition in the entire crystal. This causes the macroscopically observed rapid decrease in the MSI. The process is similar, in a sense, to the one involved in the kinetics of melting mediated by irreversible SLEF's of substantially larger threshold energies (of the order of 1–5 eV),[7(a),15] where the SLEF's break interatomic bonds. In contrast to the melting in the case considered here, SLEF-induced IA displacements $\Delta q_0 > \bar{\lambda}_\gamma$ (e.g., $\Delta q_0 = 0.2d \approx 6\bar{\lambda}$ at $d = 3$ Å and $\bar{\lambda}_\gamma = 0.1$ Å) are not accompanied by the rupture of interatomic bonds and by transition over high-energy barriers. As a result, these reversible IA displacements require the threshold energy $\Delta E_{\rm ef}$ substantially lower than the one in the melting process. Therefore, one can expect that the "transition temperature" T_0 around which the reversible SLEF's cause the rapid MSI reduction, should be substantially lower than the melting point T_M since the SLEF probability is an exponential function of the dimensionless ratio $\Delta E_{\rm ef}/kT$. This conclusion is in qualitative agreement with experimental observations.[1–4]

In order to calculate T_0 we use the approach similar to that developed for the consideration of the kinetics of phase transitions which are mediated by irreversible SLEF's.[7(a),14,15] Divide the entire solid of volume V into a large number V/V_1 of nanometer "boxes" of SLEF-related diameter $2R_1$, and volume $V_1 \approx 4R_1^3$ (Sec. III). The SLEF's of $\varepsilon_{\rm op} \geq \Delta E_{\rm ef}$ appear in random places at random instances of time. The simultaneously existing SLEF's (i.e., the SLEF's that occur within overlapping time intervals $\Delta\tau$) and LTAD's $\Delta q_0 > \bar{\lambda}_\gamma$ form the random dynamical array which exists permanently in the solid.[7(a),14,15] The SLEF-generated random dynamic array which can be seen in molecular-dynamics simulations[12,13] rapidly "migrates" in the solid; namely, every generation of the SLEF having the lifetime of the order of $\Delta\tau$ is replaced immediately by a new SLEF generation with its individual SLEF's located at places different from those in the previous generation. The mean distance between the coexisting SLEF's is[7(a),14,15]

$$\begin{aligned} r_f(\Delta E_{\rm ef}, T) &\approx [\eta_f(\Delta E_{\rm ef}, T)]^{-1/3} \\ &= d \exp\left[-\frac{\Delta S_{\rm op} + \delta S}{3k}\right] \exp\left[\frac{\Delta E_{\rm ef}}{3kT}\right] . \end{aligned} \tag{5.2}$$

At low temperatures $T^{(L)}$ when $r_f(\Delta E_{\rm ef}, T^{(L)})$ is large compared to $2R_1$, the coexisting SLEF's occupy simultaneously a small fraction $\eta_f(\Delta E_{\rm ef}, T^{(L)}) V_1 \ll 1$ of the boxes V_1. In this case the SLEF's do not interact with one another. However, when T rises, the density $\eta_{\rm ef}$ of the coexisting SLEF's increases exponentially and the distance r_f between them decreases rapidly, according to Eqs. (5.1) and (5.2). The coexisting SLEF's start to occupy neighboring boxes and thus to form clusters of the occupied boxes. The SLEF's in these clusters can correlate strongly with one another. This percolationlike dynamical process reaches its critical stage at $T_c = T_0 - \delta T$ which satisfies the condition

$$r_f(\Delta E_{\rm ef}, T_0) = 2\alpha R_i \quad \text{with } \alpha \geq 1 , \tag{5.3}$$

which is similar to that obtained in Refs. 7(a), 14, and 15. In this condition the rather large fraction α^{-3} (e.g., $\alpha^{-3} \approx 0.5$ and $\alpha \approx 1.25$) of the boxes is affected permanently by simultaneously existing SLEF's of $\varepsilon_{\rm op} \geq \Delta E_{\rm ef}$, each of which destroys the Mössbauer effect. The critical temperature T_0 calculated from Eqs. (5.2) and (5.3) is equal to

$$T_0 = \frac{\Delta E_{\rm ef}}{k}\left[\frac{\Delta S_{\rm op}}{k} + \frac{\delta S}{k} + 3\ln A\right]^{-1} . \tag{5.4}$$

Here $L = Ad$ is the average distance (at $T \approx T_0$) between the simultaneously occurring SLEF's of $\varepsilon_{\rm op} \geq \Delta E_{\rm ef} \gg kT$, $A = 2\alpha R_1/d = 3$–4 is the fitting parameter. A^3 is the number of atoms in the volume $L^3 = (Ad)^3$. Thus at temperature T_0, every volume L^3 is occupied, on the average, by a SLEF of $\varepsilon_{\rm op} \geq \Delta E_{\rm ef}$ which can reduce strongly the recoilless fraction f_M. In the next section we calculate from Eq. (5.4) numerical values of temperatures T_0 for Pb-Sn, Au-Sn, and Ag-Sn systems and show that the calculated T_0 are in good agreement with observations (Table I). Equation (5.4) is similar to that found for the melting point T_M in the SLEF-based kinetic theory of melting[7(a),15(a),15(b)] and then used for the consideration of diffusion-melting correlations in solids.[7(a),10(a),10(b)] However, the energy $\Delta E_{\rm ef}$ in Eq. (5.4) is considerably smaller than the diffusion activation energy ΔE_d entering the equation for T_M. As a result, T_0 found from Eq. (5.4) is substantially lower than T_M, in agreement with observations.[1–4]

From Eqs. (5.1), (5.2), and (5.4) we find the following relations characterizing the critical percolationlike process at T_0

$$\Delta G_{\rm ef} = 3kT_0 \ln A$$

or (5.5)

$$\Delta G_{\rm ef}/kT_0 \approx 3.3\text{–}4.15 \quad \text{for } A = 3\text{–}4 .$$

TABLE I. Calculated and experimental critical temperatures T_0 and temperature intervals δT for the anomalously rapid drop in the Mössbauer spectra intensity in some binary systems.

Systems	Calculated T_0 (K)	Experimental (obs) T_0 (K)	Calculated δT (K)	Experimental (obs) δT (K)
Pb-Sn	155	$\approx 150^{\rm a}$	18.5	$\approx 10^{\rm a}$
Au-Sn	500	$\approx 550^{\rm b}$	60	$\approx 80^{\rm b}$
Ag-Sn	880	$\approx 900^{\rm a}$	110	$\approx 150^{\rm a}$

[a] After Ref. 1 at 1% of Sn.

[b] For Au+4% Sn alloy.

Hence, one can see that the probability $W_{\mathrm{ef}}(T) \approx \Delta\tau^{1}\exp(-\Delta G_{\mathrm{ef}}/kT_0)$ of SLEF's generating LTAD's $\Delta q_0 > \bar{\lambda}_\gamma$, is large enough to cause the observed rapid decrease in the MSI. From Eqs. (3.10) and (5.5) we find the fraction of the total time per atom occupied by SLEF's able to produce LTAD's $\Delta q_0 > \bar{\lambda}_\gamma$ at T_0

$$\beta_g(\Delta E_{\mathrm{ef}}, T_0) \approx \frac{\kappa+1}{A^3} \quad \text{or } \beta_g \cong 0.5-0.2 \tag{5.6}$$

for $\kappa = 12$ (fcc crystals, e.g., Pb, Ag, and Au) and $A = 3-4$. Thus at $T \to T_0$, the SLEF-induced LTAD's affect simultaneously and persistently at least about 20–50 % of the Mössbauer atoms in the crystal that produces the observed rapid fall in the MSI. In reality, SLEF's can affect a larger fraction of the IA's, since (a) the IA's can be perturbed by SLEF's of $\varepsilon_{\mathrm{op}}^{(L)} < \Delta E_{\mathrm{ef}}$ which can also cause some reduction in the MSI not taken into account here and (b) correlations between SLEF's in neighboring boxes V_1 can also enhance the MSI reduction. These questions require a special consideration. The temperature interval δT around T_0 within which the MSI fall takes place is

$$\delta T \approx T_0/A^{3/2} \quad \text{or} \quad \delta T \approx (0.2-0.12)T_0 \tag{5.7}$$

according to Eq. (3.3) where N_1 is replaced with A^3. Equation (5.7) is in agreement with experimental observations (Table I).

VI. DISCUSSION AND COMPARISON OF THEORETICAL CALCULATIONS WITH ANOMALIES IN MÖSSBAUER EXPERIMENTS

Our dynamic SLEF-based model predicts the existence of a certain critical temperature T_0 [given by Eq. (5.4)] around which the MSI rapidly decreases within a relatively narrow temperature interval $\delta T \ll T_0$ [given by (5.7)]. The model shows that T_0 should be substantially lower than the melting point T_M of the crystal, and is also too low for atomic diffusion to occur with reasonable rates. These conclusions are in good agreement with the experimental data described in Secs. I and II.[1–4] Calculate now T_0 and δT for Pb-Sn, Au-Sn, and Ag-Sn alloys with small Sn concentrations. In order to calculate T_0 one needs to know $\Delta E_{\mathrm{ef}} = \Delta E + \delta E$, ΔS_{op}, and δS entering Eq. (5.4) where δE and δS are determined by Eqs. (3.5) and (3.6). The energy ΔE is calculated from the relation[10(b),14]

$$\Delta E = \left[\frac{\Delta q_0}{d}\right]^2 B\Omega_0 , \tag{6.1}$$

where B is bulk modulus and Ω_0 is the average volume per atom. Equation (6.1) is similar to the main equation of the phenomenological model.[20] Taking standard values for B and Ω_0 and assuming that $\Delta q_0 \approx 0.2d$ (of the order of the Lindemann amplitude), we find

$$\Delta E(\text{Pb-Sn}) = 0.32\ \text{eV}, \quad \Delta E(\text{Au-Sn}) = 0.73\ \text{eV} ,$$

and (6.2)

$$\Delta E(\text{Ag-Sn}) = 0.43\ \text{eV} .$$

In order to compute δE, δS, and ΔS_{op} we use a semiphenomenological approach since (a) large local picosecond atomic and electronic distortions caused by SLEF's in the nanometer HFP vicinity prevent us from using the effective conventional assumptions and approximations (such as assumptions on small harmonic oscillations of atoms, the separation of atomic and electronic motions, etc.) (Refs. 21–23) and (b) the detailed theory of SLEF-induced many-body picosecond phenomena in the IA nanometer vicinity is not yet completed. We apply to the SLEF-related causal nanometer polyatomic cluster some fruitful concepts proposed by Pauling and used successfully for many years in quantum chemistry of metals and polyatomic molecules.[24–26] We make use of the fact that this causal cluster containing a few tens of atoms is similar, in a sense, to a polyatomic molecule.

Consider Pauling electronegativities of Sn, Pb, Au, and Ag atoms

$$\begin{gathered} f(\text{Sn}) = 1.96 , \\ f(\text{Pb}) = 2.33 , \\ f(\text{Au}) = 2.54 , \\ \text{and} \\ f(\text{Ag}) = 1.93 . \end{gathered} \tag{6.3}$$

Differences between f(Sn) and those of the host atoms

$$\begin{gathered} \Delta f(\text{Pb-Sn}) = 0.37 , \\ \Delta f(\text{Au-Sn}) = 0.57 , \\ \text{and} \\ \Delta f(\text{Ag-Sn}) \to 0 \end{gathered} \tag{6.4}$$

are associated with the corresponding percent of ionic character of single bonds

$$\begin{gathered} \Delta i(\text{Pb-Sn}) = 3.7 \times 10^{-2} , \\ \Delta i(\text{Au-Sn}) = 7 \times 10^{-2} , \\ \text{and} \\ \Delta i(\text{Ag-Sn}) \to 0 . \end{gathered} \tag{6.5}$$

A. The Pb-Sn system with $f(\text{Pb}) > f(\text{Sn})$

Substantial differences Δf(Pb-Sn) and Δi(Pb-Sn) in f and i between Pb and Sn atoms cause the local redistribution of valence electrons (of Sn and surrounding Pb atoms) in space and energy in the nanometer vicinity of Sn atoms. In the absence of the SLEF's this redistribution which "equilibrates" the local electron energy levels of the Sn impurity and the surrounding Pb atoms is associated with (a) shifts of the local energy levels of the Sn and Pb atoms in opposite directions and (b) partial delocalizations of four valence electrons of the Sn atom in the Sn vicinity of radius

$$r_i \approx (\hbar^2/m|\langle \delta e \rangle|)^{1/2} = \gamma_i d . \tag{6.6}$$

Here m is the electron mass, γ_i is the parameter considered below. During the SLEF lifetime $\Delta\tau$ the four valence electrons of the Sn atom reduce their localization radius from r_i to the value $r_f=2d$ (of the order of the size of the transient point defect), and they experience downward transitions and release the energy $|\delta E|=4\langle\delta e\rangle$. Here the number of downward electron transitions per SLEF is $\Delta n^d=4$, and the negative change in the local configurational entropy associated with the downward electron transitions is

$$\delta S=-4\ln\left[\frac{\Gamma_i}{\Gamma_f}\right] \quad \text{or} \quad \delta S=-12\ln(\gamma_i/2)\ . \tag{6.7}$$

Here $(\Gamma_i/\Gamma_f)\cong(r_i/r_f)^3\approx\gamma_i^3/8$ is the ratio of the initial Γ_i and final Γ_f statistical weights of the electrons involved determined, mainly, by the volumes $V_i=4r_i^3$ and $V_f=4r_f^3$ similar to that discussed in [11].

We now calculate the energy $\langle\delta e(\text{Pb-Sn})\rangle$ [entering Eqs. (3.5)–(3.10), (4.5), (4.6), (5.4), and (6.6)] using the following empirical equation:

$$|\langle\delta e(\text{Pb-Sn})\rangle|=[|\langle\delta e(\text{Pb})\rangle||\langle\delta e(\text{Sn})\rangle|]^{1/2}\ , \tag{6.8}$$

which is like those proposed by Pauling and used successfully for bond energy calculations.[21–23] We use the following relations $|\langle\delta e(\text{Pb})\rangle|\approx kT_M(\text{Pb})$ and $|\langle\delta e(\text{Sn})\rangle|\approx kT_M(\text{Sn})$ similar to those successfully applied earlier for various materials and processes, including those in Pb, Au, and Ag.[7(a),10(a),10(b)] We shall see below that the above relations lead to a good agreement with observations. From Eqs. (6.7) and (6.8) and standard melting temperatures for Pb and Sn one finds

$$|\langle\delta e(\text{Pb-Sn})\rangle|\approx k\,[T_M(\text{Pb})T_M(\text{Sn})]^{1/2} \approx 0.047\ \text{eV}\ . \tag{6.9}$$

The same result one finds from another empirical equation

$$|\langle\delta e(\text{Pb-Sn})\rangle|\approx 0.5\Delta U(\text{Pb-Sn})\approx 0.048\ \text{eV}\ . \tag{6.10}$$

Here

$$\Delta U(\text{Pb-Sn})\approx\Delta i(\text{Pb-Sn})[E_B(\text{Pb})E_B(\text{Sn})]^{1/2} \tag{6.11}$$

is the energy difference per one of four valence electrons of Sn atoms where the Pauling idea of geometrical average of individual bonding energies $E_B(\text{Pb})$ and $E_B(\text{Sn})$ of Pb and Sn atoms is used. The factor 0.5 in Eq. (6.11) takes into account the shifts in the opposite directions of energy levels in the Sn vicinity mentioned above. Using the value $|\langle\delta e\rangle|\approx 0.047$ eV, one finds [from Eq. (6.6)] $\gamma_i\approx 3.4$ and, therefore, $r_i\approx 3.4d(\text{Pb})\approx 11.5$ Å. Then one finds [from Eq. (6.7)] $\delta S\approx -6.7k$.

The delocalization of the four valence electrons of Sn atoms within their vicinities of radius $r_i\approx 3.4d(\text{Pb})$ reduces the effective radius $\tilde{\rho}_c(\text{Sn})$ of Sn atoms in the Pb lattice. As a result, $\tilde{\rho}_c(\text{Sn})$ becomes smaller than the Sn covalent radius $\rho_c(\text{Sn})=1.41$ Å which is, in turn, smaller than that $\rho_c(\text{Pb})=1.47$ Å for Pb atoms. Thus the delocalization of the valence electrons of the Sn atoms enhances the "freedom" for the motion of the Sn atoms within the "cages" in the Pb crystal where they are located. The relatively large "cages" within which Sn atoms can move in the PB crystal are favorable for large SLEF-induced reversible LTAD's $\Delta q_0>\lambda_\gamma$ of Sn atoms that can occur at relatively low SLEF energies:

$$\varepsilon_{\text{op}}\geq\Delta E_{\text{ef}}(\text{Pb-Sn}) =E(\text{Pb-Sn})-|\delta E(\text{Pb-Sn})|\approx 0.14\ \text{eV}\ , \tag{6.12}$$

where $\delta E(\text{Pb-Sn})\approx -4|\langle\delta e(\text{Pb-Sn})\rangle|\approx -0.18$ eV.

The small value of $\Delta E_{\text{ef}}(\text{Pb-Sn})$ leads to low $T_0(\text{Pb-Sn})$ [according to Eq. (5.4)]. This conclusion is in agreement with observations. Besides, the relatively small effective radius of Sn atoms in the Pb lattice is favorable for large SLEF-induced local disordering and a high disordering entropy in the vicinity of the Sn atom which is

$$\Delta S_{\text{op}}\approx(\kappa+1)k \quad \text{or} \quad \Delta S\approx 13k \quad \text{for } \kappa=12\ . \tag{6.13}$$

Then one finds from Eq. (5.4) the temperature $T_0(\text{Pb-Sn})\approx 155$ K that is in good agreement with observations (Table I).

B. The Au-Sn system

Consider now the Au-Sn system which can be treated quite similarly to the Pb-Sn one. Since $f(\text{Au})>f(\text{Sn})$ [Eq. (6.3)], the four valence electrons of the Sn atoms are delocalized in their nanometer vicinities and this causes the corresponding reduction of the effective radius of Sn atoms in the Au-Sn system. Here the energy parameter $\langle\delta e(\text{Au-Sn})\rangle$ is calculated from the relation

$$|\langle\delta e(\text{Au-Sn})\rangle|\approx k\,[T_M(\text{Au})T_M(\text{Sn})]^{1/2} \approx 0.071\ \text{eV} \tag{6.14}$$

[similarly to Eqs. (6.8) and (6.9)], where $T_M(\text{Au})=1337$ K and $T_M(\text{Sn})=505$ K are the melting points of Au and Sn, respectively. Through calculations like those considered above for the Pb-Sn system we find [from Eq. (5.4)] the critical temperature $T_0(\text{Au-Sn})\approx 500k$ which is in agreement with experimental observations (Table I). Here $\delta S(\text{Au-Sn})\approx -6.7k$ and $\delta E(\text{Au-Sn})\approx -0.28$ eV.

C. The Ag-Sn system

Consider now the Ag-Sn system. In this case, the local properties in the vicinity of the Sn atom are substantially different from those in the Pb-Sn and Au-Sn systems. From Eqs. (6.3)–(6.5) one can see that

$$f(\text{Ag})\approx f(\text{Sn}),\quad \Delta f(\text{Ag-Sn})\to 0 \quad \text{and} \quad \Delta i(\text{Ag-Sn})\to 0\ . \tag{6.15}$$

Hence one finds that

$$\delta E(\text{Ag-Sn})\to 0\ , \quad \delta S(\text{Ag-Sn})\to 0\ , \tag{6.16}$$

and

$$\Delta E_{\rm ef}(\text{Ag-Sn}) \rightarrow E(\text{Ag-Sn}) \approx 0.43 \text{ eV} .$$

Therefore, in the Ag-Sn system, the partial delocalization of the valence electrons of Sn atoms and the corresponding reduction of the effective radius of Sn atoms do not take place contrary to those occurring in the Pb-Sn and Ag-Sn systems. This causes an increase of $\Delta E_{\rm ef}$ and the critical temperature T_0(Ag-Sn) since downward electron transitions which reduce $\Delta E_{\rm ef}$, do not occur and $\delta E \rightarrow 0$. Besides, the covalent radius $\rho_c(\text{Ag}) = 1.34$ Å of Ag atoms is smaller than $\rho_c(\text{Sn}) = 1.41$ Å of Sn atoms and this radius is not reduced by the partial delocalization of the Sn valence electrons. Therefore the substitutional "cage" for the Sn atom in the Ag lattice is smaller than the Sn atom itself. This creates a local compression in the Sn vicinity. As a result, the Sn atom has to experience a SLEF of relatively high $\varepsilon_{\rm op} \geq \Delta E(\text{Ag-Sn})$ in order to get the displacement $\Delta q_0 > \lambda_\gamma$ sufficient to destroy the Mössbauer effect. Such a specific local situation in the Sn vicinity reduces substantially local SLEF-induced disordering and the corresponding entropy increase $\Delta S_{\rm op}$(Ag-Sn) during the LTAD's Δq_0. Thus, only the Sn atom and, perhaps, one or two of the nearest neighbors located along the direction of its displacement, are involved in the significant local disordering. Thus one finds $\Delta S_{\rm op}(\text{Ag-Sn}) \approx (1-2)k$. This relatively small $\Delta S_{\rm op}$ (compared to their counterparts in the Pb-Sn and Au-Sn systems) decrease the denominator in Eq. (5.4) and increase T_0(Ag-Sn). The facts mentioned above lead to the relatively high critical temperature $T_0(\text{Ag-Sn}) \approx 880$ K in agreement with observations (Table I).

Using the calculated temperatures T_0 for the Pb-Sn, Ag-Sn, and Au-Sn systems one finds from Eq. (5.7) temperature intervals within which the MSI rapid fall takes place (for $A = 4$)

$$\delta T(\text{Pb-Sn}) \approx 18.5 \text{ K} ,$$

$$\delta T(\text{Au-Sn}) \approx 62 \text{ K} , \tag{6.17}$$

and

$$\delta T(\text{Ag-Sn}) \approx 110 \text{ K} .$$

These values are also in agreement with experimental results (Table I).

Our kinetic model of the anomalous MSI temperature behavior predicts the existence of the critical concentration of impurity

$$a_M^{(0)} \approx \frac{1}{A^3} \quad \text{or } a_M^{(0)} \approx 3.5-1.5\,\% \tag{6.18}$$

(for $A = 3-4$) which satisfies the following conditions: (i) For lower IA concentrations $a_M^{(L)} < a_M^{(0)}$ the temperature T_0 [given by Eq. (5.4)] is independent of $a^{(L)}$ and (ii) for higher IA concentrations $a_M^{(H)} > a_M^{(0)}$ the temperature T_0 increases when $a_M^{(H)}$ becomes larger. These conclusions, which are in agreement with experimental data,[1-4] result from the fact that the SLEF-related regions involved in formation of simultaneously occurring SLEF's are not overlapped for lower $a_M^{(L)} \approx (\Delta\rho_M^{(L)})^{-3}$ which satisfy the following condition:

$$\Delta\rho_M^{(L)} > \Delta\rho_M^{(0)} \approx Ad \approx 4d , \tag{6.19}$$

where $\Delta\rho^{(0)} \approx d/(a_M^{(0)})^{1/3}$. For higher concentrations $a_M^{(H)} = (\rho_M^{(H)})^{-3} > a_M^{(0)}$ (where $\Delta\rho_M^{(H)} < Ad$) the SLEF-related regions associated with the simultaneously occurring SLEF's can overlap. This reduces the probability of SLEF's and SLEF-induced IA displacements $\Delta q_0 > \lambda_\gamma$ (other conditions unchanged) since more than one SLEF using the same "nanometer energy reservoir" (of a limited energy) to be formed. Consequently, the temperature T_0 [Eq. (5.4)] increases when $a_M^{(H)}$ becomes larger and $\Delta\rho_M^{(H)} < Ad$ decreases. In order to describe the dependence of T_0 on $a_M^{(H)}$ (at small $a_M^{(H)} \ll 1$) one can suggest the following empirical relation:

$$T_0(a_M^{(H)}) = T_0(a_M^{(0)}) + b\,(a_M^{(H)} - a_M^{(0)}) . \tag{6.20}$$

Here b is the fitting parameter which should be found from experimental data. For instance, for the Pb-Sn system one finds $b = 25$ K/1% from the experimental data for $a_M^{(0)} = 1\%$ and $a_M^{(H)} = 2\%$.[1] Then using the value of $b = 25$ K/1%, one can calculate $T_0(a_M^{(H)} = 3\%) = 200$ K, in agreement with observations.

VII. SUMMARY

A dynamical many-body electron-related model for anomalous fluctuation-induced temperature dynamics of impurities in nanometer environment is presented. This model is applied to the explanation of experimental anomalies observed in Mössbauer spectroscopy. The model considers reversible large transient atomic displacements (LTAD's) Δq_0 of impurity atoms (in particular, of Mössbauer emitters) generated by short-lived large energy fluctuations (SLEF's) of single atoms (or of few-body clusters of $N_0 \gtrsim 1$ atoms) of lifetime $\Delta\tau = 10^{-13}-10^{-12}$ s. Reversible atomic SLEF's and LTAD's can cause the observed rapid fall in the Mössbauer spectral intensity (MSI). The SLEF's supply fluctuating atoms with the thermal energy $\varepsilon_{\rm op} \geq \Delta E_{\rm ef} \gg kT$ sufficient to initiate the LTAD's $\Delta q_0 > \lambda_\gamma$ which, in turn, cause destructive interference of γ emission of impurity atoms (IA's) of wavelength λ_γ, that destroys the recoilless γ emission. This model suggests a dynamical explanation of the observed anomalously rapid decrease in the MSI within a relatively narrow temperature interval $\delta T \ll T_0$ around a certain temperature T_0. Here T_0 is substantially lower than the melting point T_M and lower than temperatures at which atomic diffusion has a marked influence.

The model is based on the kinetic many-body theory of SLEF's of atomic particles and SLEF-induced processes in solids. This model takes into account reversible picosecond atomic and electronic processes induced by reversible SLEF's in nanometer vicinities of IA's. The reversible SLEF-induced displacements $\Delta q_0 > \lambda_\gamma$ of IA's are not accompanied by transitions of fluctuating atoms over energy barriers, since the SLEF threshold energy $\Delta E_{\rm ef}$ is lower than the diffusion barrier energies. The SLEF-induced phenomena are accompanied by the reversible picosecond disordering, and an increase in the local entropy in the nanometer IA vicinity.

Around a certain temperature T_0 the probability of the LTAD's $\Delta q_0 > \lambda_\gamma$ and simultaneously existing reversible SLEF's and LTAD's become so large that they cause the observed anomalously sharp drop in the MSI within the temperature interval $\delta T \ll T_0$. The temperatures T_0 and δT are calculated and expressed in terms of material parameters which characterize the local picosecond atomic and electronic processes induced by reversible SLEF's in the IA nanometer vicinity. The calculated T_0 and δT are in good agreement with their experimental counterparts observed in the Pb-Sn, Au-Sn, and Ag-Sn systems (see Table I). The model suggests a qualitative explanation for the observed increase in T_0 with concentration a_M of impurity atoms. The critical concentration $a_M^{(0)}$ of IA's above which T_0 arises with a_M is considered. An empirical equation describing the observed dependence of T_0 on a_M is suggested. The proposed model describing the SLEF-induced dynamics of IA's and their nanometer environment which cause the observed MIS anomalies is more general than the phenomenological model described in Refs. 1–4. Effects caused by the reversible SLEF's and LTAD's are expected to be seen in EXAFS experiments which are consistent with the MSI anomalies.[1] One can also expect that some other effects related to reversible SLEF's and LTAD's can be observed through techniques other than the MSI and EXAFS.

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