WIDTH AND SHAPE OF MÖSSBAUER LINES IN SOLID SOLUTIONS

M. A. KRIVOGLAZ

Institute of Metal Physics, Academy of Sciences, Ukrainian S.S.R.

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The Mössbauer effect in solid solutions is studied. We take into account explicitly the dependence of the change in vibrational energy, which is associated with the change in mass of the emitting or absorbing nucleus, on the configuration of the atoms of different types surrounding this nucleus. An estimate is made of the resulting broadening of the Mössbauer line. The line shape in solid solutions is considered for the limiting cases of large and small natural width. Other causes of broadening of the Mössbauer line in solid solutions are mentioned.

THE position of the line from no-phonon absorption or emission of photons by nuclei in a crystal (the Mössbauer line^[1]) depends slightly on temperature.^[2,3] This dependence results from the small difference in masses of the nuclei in their ground and excited states, which leads to a difference in the vibrational energy E_n of the lattice in the initial and final states, even when the oscillator quantum numbers n are not changed. In ideal crystals the same energy difference E_n appears for excitation of any nucleus in the lattice so that, as shown by Snyder and Wick,^[4] there is only a shift of the line but no broadening. In solid solutions, however, this change in energy E_n must depend on the type of atom located in the neighborhood of the radiating (or absorbing) nucleus. Thus the position of the maximum of the Mössbauer line will be different for different configurations of the atoms in the solution surrounding the radiating nucleus, and the resulting spectral distribution should be broadened in accordance with the numerous different configurations around the radiating nucleus. In the present paper we treat the width and shape of such a spectral distribution.

Let us consider a binary substitutional solution A - B, in which photons can be emitted (absorbed) by the nuclei A. To simplify the formulas, we shall restrict ourselves to the case where the relative difference in masses of the component atoms is much greater than the difference in the interatomic force constants, and shall not take the latter effect into account. Then the problem reduces to finding the change δE_n in the vibrational energy when the mass of the s-th atom A changes by $\delta m = \Delta E/c_1^2$ (where ΔE is the difference in energy of the nucleus in the ground and excited

states, and c_1 is the velocity of light) as a function of the distribution of masses m_A and m_B on the other lattice sites s. We shall characterize the distribution of A and B atoms over the lattice sites by giving the numbers c_s , which are equal to 1 or 0, according as the site s is occupied by an A or by a B atom. The dependence of the vibration energy change on configuration is then determined by the dependence of δE_n on the variables c_s . This dependence can be found explicitly for the case of small mass difference of the atoms, or when the concentration of one of the components is low.

It is obvious that

$$\delta E_n = \frac{\partial E_n}{\partial m_{s'}} \, \delta m = \left(\psi_n^* \frac{\partial H}{\partial m_{s'}} \, \psi_n \right) \delta m = \frac{\hbar^2 \delta m}{2m_A^2} \, (\psi_n^* \Delta_{s'} \psi_n),$$

where H is the oscillation Hamiltonian and $\Delta_{S'}$ is the Laplacian for the atom s'. For sufficiently small $m_A - m_B$, no local oscillations appear in the crystal. According to ^[4], we do not have to take account of fluctuations of the oscillator quantum numbers, and can replace these quantum numbers by their average values in the final expression for δE_n . Obviously we can then write δE_n in the form

$$\delta E_n = \frac{1}{2} \hbar^2 m_A^{-2} \delta m \operatorname{Sp} \left[\Delta_{s'} e^{-\lambda H} \right] \left[\operatorname{Sp} e^{-\lambda H} \right]^{-1}, \tag{1}$$

where $\lambda = 1/kT$, and the trace is taken over the complete system of oscillation wave functions for a given configuration of A and B atoms.

As the zeroth approximation for the problem of oscillation of a solid solution containing atoms of different masses we choose a crystal with the average reciprocal mass of the atoms $m^{-1} = m_s^{-1}$. We assume that there is one atom in the unit cell

of such a crystal. The Hamiltonian for the vibrations of the solid solution is expressed in terms of the phonon creation and annihilation operators a_{kj}^{\dagger} , a_{kj} (where k is the wave vector and j the branch number) as follows (cf., for example, ^[5]):

$$H = \frac{1}{2} \sum_{\mathbf{k}j} \hbar \omega_{\mathbf{k}j} \left(a_{\mathbf{k}j}^{+} a_{\mathbf{k}j} + a_{\mathbf{k}j} a_{\mathbf{k}j}^{+} \right) + H',$$

$$H' = \frac{1}{2} \sum_{\mathbf{k}j\mathbf{k}'j'} V_{\mathbf{k}j\mathbf{k}'j'} a_{\mathbf{k}j} a_{\mathbf{k}'j'}^{+} + \frac{1}{2} \sum_{\mathbf{k}j\mathbf{k}'j'} V_{\mathbf{k}j\mathbf{k}'j'} a_{\mathbf{k}j} a_{\mathbf{k}'j'}^{+} + \text{H.c.}$$
(2)

Here

$$V_{\mathbf{k}j\mathbf{k}'j'} = \frac{\hbar}{2N} \frac{(m_B - m_A)m}{m_A m_B} \sqrt{\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'}} (\mathbf{e}_{\mathbf{k}j} \mathbf{e}_{\mathbf{k}'j'}^*) \sum_{\mathbf{s}} (c_{\mathbf{s}} - c)$$
$$\times \exp[i(\mathbf{k} - \mathbf{k}')\mathbf{R}_{\mathbf{s}}], \qquad (3)$$

N is the number of atoms, $e_{kj}^* = -e_{-kj}^*$ are polarization unit vectors, c is the concentration of A atoms. The expression for $V'_{kjk'j'}$ is obtained from (3) by replacing k' by -k'. Similarly, the operator $\hbar^2 \delta m (2m_A^2)^{-1} \Delta_{s'}$ is expressed in terms of a_{kj}^* , a_{kj} by formula (2) for H', if we replace

$$(\mathbf{m}_{A} - \mathbf{m}_{B}) \sum_{\mathbf{s}} (\mathbf{c}_{\mathbf{s}} - \mathbf{c}) \exp[\mathbf{i}(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}_{\mathbf{s}}]$$
 by
$$\frac{m_{B}}{m_{A}} \delta m \exp[\mathbf{i}(\mathbf{k} - \mathbf{k}') \mathbf{R}_{\mathbf{s}'}]$$

in expression (3) for Vkjk'j'.

Substituting the expressions for H and $\Delta_{S'}$ in (1), expanding the exponential operator in series in H' and stopping with the linear terms, we can easily compute the trace in (1). As a result we find that, to terms of order $\delta m (m_A - m_B)$ inclusive, δE_n can be represented as a linear form in the c_s :

$$\delta E_n = \hbar \alpha^0 + \sum_{s \neq 0} \hbar \alpha_s (c_s - c).$$
(4)

Here

$$\alpha_{s} = \frac{1}{4N^{2}} \frac{m_{A} - m_{B}}{m} \frac{\delta m}{m} \sum_{\mathbf{k}/\mathbf{k}'j'} \omega_{\mathbf{k}/\omega\mathbf{k}'j'} |\mathbf{e}_{\mathbf{k}/\mathbf{e}_{\mathbf{k}'j'}}|^{2} \cos{(\mathbf{k} - \mathbf{k}', \mathbf{R}_{s})}$$

$$\times \left[\frac{n_{\mathbf{k}j} - n_{\mathbf{k}'j'}}{\omega_{\mathbf{k}j} - \omega_{\mathbf{k}'j'}} - \frac{1 + n_{\mathbf{k}j} + n_{\mathbf{k}'j'}}{\omega_{\mathbf{k}j} + \omega_{\mathbf{k}'j'}} \right],\tag{5}$$

$$\alpha^{0} = -\frac{m\delta m}{2m_{A}^{2}N}\sum_{\mathbf{k}j}\omega_{\mathbf{k}j}\left(n_{\mathbf{k}j}+\frac{1}{2}\right) + \alpha_{0},$$

where the n_{kj} are the average quantum numbers of the oscillators kj, α_0 is the value of α_s for $R_s = 0$, and the coordinate origin is taken at the site s'.

If the mass difference of the atoms is large, but the concentration of one of the components is so small that we can neglect configurations in which there are two (or more) impurity atoms in the neighborhood of the given site, then δE_n can again be written as the linear expression (4) in the c_s . The quantities α^0 , α_s appearing in this expression are, however, not given by formulas (5) in this case, but rather by more complicated formulas, which can be found without the use of perturbation theory by the methods which have been applied in numerous papers.^[6]

The dependence of the change in vibrational energy δE_n on the atom configuration (on the c_s) results in a broadening of the Mössbauer line. Obviously the intensity distribution will be qualitatively different in those cases where this broadening is much larger or much smaller than the natural width Γ . First let us consider the case where the broadening is much greater than Γ , and set $\Gamma = 0$. Then the spectral distribution of the intensity of the no-phonon emission of photons with wave vector **q** by the nucleus s', per unit solid angle and per unit frequency range, is given by the formula

$$\sigma (\mathbf{q}, \ \omega) = \frac{\sigma^{o}}{4\pi c} \langle c_{s'} D\delta (\omega - \delta E_{n}/\hbar) \rangle$$

= $\frac{\sigma^{o}}{4\pi c} \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle c_{s'} D \exp (-i\delta E_{n}t/\hbar) \rangle,$ (6)
$$D = \exp \left[-M_{s'}(c_{s}, \mathbf{q})\right].$$

Here σ^0 is the integral intensity of emission in the absence of vibration, D is the Debye factor for attenuation of the intensity of the no-phonon emission for the site s', ω is measured from the frequency $\Delta E/\hbar$, corresponding to the unshifted emission line, $\langle \ldots \rangle$ denotes an average over all possible configurations of atoms on the lattice sites. Like δE_n , D also depends on the configuration of the atoms around the site s'. But the differences in D for different configurations are proportional to $m_A - m_B$. Thus in determining the spectral distribution, neglecting terms $\sim (m_A - m_B)^2$, we can take D with the average value $\exp[-M_A(q)]$.

The spectral shape is conveniently characterized by giving the moments of the function $\sigma(\mathbf{q}, \omega)$. Substituting (4) in (6) and integrating by parts, we find that the moments are given by the formulas

$$\sigma_{m}(\mathbf{q}) = \int (\omega - \alpha^{0})^{m} \sigma(\mathbf{q}, \omega) d\omega;$$

$$\sigma_{0}(\mathbf{q}) = \int \sigma(\mathbf{q}, \omega) d\omega = \frac{\sigma^{0}}{4\pi} \exp[-M_{A}(\mathbf{q})];$$

$$\sigma_{m}' = \frac{\sigma_{m}(\mathbf{q})}{\sigma_{0}(\mathbf{q})} = \frac{1}{c} \langle c_{s'} \left[\sum_{s \neq 0} \alpha_{s}(c_{s} - c) \right]^{m} \rangle \quad (7)$$

(the site s' is at the origin of coordinates). Formulas (7) express the moments in terms of the constants α_s , the concentration, and the correlation parameters. In the case of an ideal solution, where there is no correlation, $\langle c_s^m \rangle = c$, $< c_{s_1}^{m_1} c_{s_2}^{m_2} > = c^2 (s_1 \neq s_2)$ etc, and it is easy to obtain expressions which give explicitly the concentration dependence of the first few moments:

$$\sigma'_{1} = 0, \qquad \sigma'_{2} = c \left(1 - c\right) \sum_{s \neq 0} \alpha_{s}^{2}, \quad \sigma'_{3} = c \left(1 - c\right) \left(1 - 2c\right) \sum_{s \neq 0} \alpha_{s}^{3}$$

$$\sigma'_{4} = c \left(1 - c\right) \left(1 - 3c + 3c^{2}\right) \sum_{s \neq 0} \alpha_{s}^{4} + c^{2} \left(1 - c\right)^{2} \sum_{s_{1,2} \neq 0, \ s_{1} \neq s_{2}} \alpha_{s_{1}}^{2} \alpha_{s_{2}}^{2}$$
(8)

The first moment σ'_1 determines the average frequency of the emitted radiation. Since $\sigma'_1 = 0$, in ideal solutions the shift of the average frequency resulting from the change δm in the mass of the radiating nucleus is determined by the quantity α^0 . Except for a numerical factor which is almost equal to one, the value of $\sqrt{\sigma_2}$ is equal to the halfwidth δ of the spectral curve. It follows from (8) that, in the case we are considering, the concentration dependence of the half-width of the curve is determined by the factor $\sqrt{c(1-c)}$. At high temperatures, according to (5) and (8), the halfwidth is proportional to T, and as $T \rightarrow 0$ it tends to a nonzero limit. The third moment σ'_3 determines the asymmetry of the spectral distribution. In ideal solutions with stoichiometric composition $(c = \frac{1}{2})$, the asymmetry disappears, but for other concentrations the asymmetry index is different from zero and must have opposite sign for $c > \frac{1}{2}$ and $c < \frac{1}{2}$. The spectral curve is then obviously significantly different from the Lorentz shape.

For a rough estimate of the order of magnitude of the broadening δ , we consider, for example, solutions with a face-centered cubic lattice, and include in the sum over s for σ'_2 only the terms corresponding to the first and second coordination spheres (for large R_S , α_S falls off like R_S^{-7}). For T = 0, in the Debye approximation, it follows from (5) that

 $\alpha_1 \ll \alpha_2, \qquad \alpha_2 \sim -\frac{1}{3} \cdot 10^{-2} \omega_m \frac{\Delta m \delta m}{m} \sim \frac{2}{3} \cdot 10^{-2} \alpha^0 \frac{\Delta m}{m}$ ($\Delta m = m_A - m_B, \omega_m$ is the maximum vibration frequency, α^0 is the line shift). From this it follows that δ is of order

$$\delta \sim 2\sqrt{z_2}\sqrt{c(1-c)} \alpha_2 \sim 0.03\sqrt{c(1-c)} \alpha_0 \Delta m/m$$

(where z_2 is the coordination number). Since the value of α^0 varies between the limits $\hbar\alpha^0 \sim 10^{-9}$ - 3×10^{-8} ev, in concentrated solutions ($c \sim \frac{1}{2}$) with large relative mass difference of the atoms ($|\Delta m| \sim m$) the width can be of order $\delta \sim 10^{-10}$ - 10^{-9} ev. Thus δ can be much greater than the natural width Γ only for the narrowest lines, such as for example Zn^{67} ($\Gamma = 5 \times 10^{-11}$ ev). We should note that the use of the true vibration spectrum in place of the Debye spectrum in evaluating the sums (5) may change this estimate. In the case of nonideal solutions, the moments depend not only on the concentration but also on the parameters determining the degree of order in the solution. For example, when there is short range order in disordered solutions, the first moment, according to (7), is given by the formula

$$\sigma_1 = \sum_{s \neq 0} (p_s - c) \alpha_s, \qquad (9)$$

where p_S is the a posteriori probability of finding an A atom at site s if there is an A atom at the origin. Thus when short range order is established in a solution one may observe a significant shift in the Mössbauer line. Similarly, short range order may affect the width and shape of the line. We also see from (7) that the second and higher moments depend on the parameters for short range order for three and more sites.

The establishment of long range order may have an even more marked influence on the Mössbauer effect. To be specific, let us consider solutions with a body-centered cubic lattice, like β -brass (CsCl type). When long range order is present, the probabilities of occupying sites of the first and second types with A atmos are different: $p_A^{(1)}$ = $c + \eta/2$ and $p_A^{(2)} = c - \eta/2$ (where η is the degree of long range order). In the case of an ordered solution, the energy change δE_n given by (4) is conveniently written as

$$\delta E_n = \hbar \alpha^0 + \hbar \alpha^{\pm} + \sum_{s \neq 0} \hbar \alpha_s (c_s - \bar{c}_s).$$

Here \overline{c}_s is equal to $p_A^{(1)}$ or to $p_A^{(2)}$, depending on the type of the site s;

$$\alpha^{\pm} = \pm \frac{1}{2} \eta \left(\sum_{s \neq 0} \alpha_s - \sum_s \alpha_s \right),$$

where the plus sign corresponds to a radiating nucleus on a site of the first type, and the minus sign to one on a site of the second type; the summation Σ'' goes over even coordination spheres, the sum Σ' over odd ones.

For the case of large values of η , the correlation in the solution is unimportant. Neglecting correlations, we can easily determine the moments for the spectral curves corresponding to radiation by nuclei on sites of the first and second types, in the same way as we did above, and then we can find the moments for the resulting intensity distribution by combining the results. The first moment is equal to

$$\sigma_1' = \frac{\eta^2}{4c} \Big(\sum_{s \neq 0}^{n'} \alpha_s - \sum_{s}^{\prime} \alpha_s \Big).$$
 (10)

Thus the shift of the average frequency ω relative to α^0 when long range order is established, is proportional to η^2 . The second moment, defined relative to the average frequency $\alpha_0 + \sigma_1'$ (the dispersion of the curve) is equal to

$$\begin{aligned} \sigma_{2}^{'} &= \frac{1}{\sigma_{0}(\mathbf{q})} \int \left(\omega - \alpha^{0} - \sigma_{1}^{'} \right)^{2} \sigma\left(\mathbf{q}, \omega\right) d\omega \\ &= \frac{1-c}{c} p_{A}^{(1)} p_{A}^{(2)} \sum_{s}^{\prime} \alpha_{s}^{2} + \frac{1}{2c} \left[(p_{A}^{(1)})^{2} \left(1 - p_{A}^{(1)} \right) \right. \\ &+ \left(p_{A}^{(2)} \right)^{2} \left(1 - p_{A}^{(2)} \right) \left[\sum_{s\neq 0}^{\prime} \alpha_{s}^{2} \right. \\ &+ \frac{\eta^{2}}{4c^{2}} p_{A}^{(1)} p_{A}^{(2)} \left(\sum_{s}^{\prime} \alpha_{s} - \sum_{s\neq 0}^{\prime \prime} \alpha_{s} \right)^{2}. \end{aligned}$$
(11)

For solutions with stoichiometric composition ($c = \frac{1}{2}$), this formula simplifies:

$$\sigma_{2}' = \frac{1}{4} (1 - \eta^{2}) \sum_{s \neq 0} \alpha_{s}^{2} + \frac{1}{4} \eta^{2} (1 - \eta^{2}) \left(\sum_{s}' \alpha_{s} - \sum_{s \neq 0}'' \alpha_{s} \right)^{2}.$$
(12)

As it should be, with ordering of the solution, when $\eta \rightarrow 1$, the dispersion and width of the curve tend to zero.

Let us now take into account the finite value of the natural width Γ of the emission line. Expression (4) then determines the positions of the maxima of the Lorentz curves with width Γ for the different atom configurations in the solution. For nonzero, but small, Γ ($\Gamma \ll \delta$) it is obvious that the spectral curve in the region of the maximum $|\omega - \alpha^0| \leq \delta$ is only slightly smeared out. However, including the finite value of Γ essentially changes the spectral distribution in the "skirts" of the curve, for $|\omega - \alpha^0| \gg \delta$. Whereas, when $\Gamma = 0$, the quantity $\sigma(\mathbf{q}, \omega)$ falls off faster than any power of $1/\omega$ (all the moments $\sigma_{\mathbf{m}}$ are finite), for $\Gamma \neq 0$, in the region $|\omega - \alpha^0| \gg \delta$ the quantity $\sigma(\mathbf{q}, \omega) \approx \sigma_0 \Gamma |2\pi (\omega - \alpha^0)^2|^{-1}$ falls off like $(\omega - \alpha^0)^{-2}$.

It is easy to see that including the finite width Γ in the integral representation (6) for $\sigma(\mathbf{q}, \omega)$ reduces to adding the factor $\exp(-\Gamma |\mathbf{t}|/2)$. In particular, for ideal solutions, performing the average, we get

$$\sigma(\mathbf{q},\omega) = \sigma_0 \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp\left\{i\left(\omega - \alpha^0 + c\sum_{s\neq 0} \alpha_s\right)t\right\}$$
(13)
$$\times \prod_{s\neq 0} \left[1 - c + ce^{-i\alpha_s t}\right] \exp\left(-\Gamma |t|/2\right).$$

Performing the integration, we can represent $\sigma(\mathbf{q}, \omega)$ as a sum of Lorentz curves:

$$\sigma(\mathbf{q},\omega) = \frac{\sigma_0}{2\pi} \sum_{\dots,\rho_i \dots} A_\rho \Gamma \left\{ \left[\omega - \alpha^0 - \sum_{i=1}^{\infty} \alpha_i \left(p_i - cz_i \right) \right]^2 + \Gamma^2 / 4 \right\}^{-1}.$$
(14)

Here i is the number of the coordination sphere; α_i is the value of α_s for the i-th sphere; $p_i = 1, 2, ..., z_i$, z_i are the coordination numbers;

$$A_{p} = \prod_{i=1}^{\infty} \frac{z_{i}!}{p_{i}! (z_{i} - p_{i})!} c^{p_{i}} (1 - c)^{z_{i} - p_{i}}$$

The superposition of Lorentz curves (14) usually describes a smooth spectral distribution. Only in special cases, when Γ is very small and the concentration of one of the components is low (or the solution is almost completely ordered) can one observe the fine structure of this distribution, which is given for ideal solutions by formula (14). The shape of the smooth curve which is obtained for $\sigma(\mathbf{q}, \omega)$ when Γ is small ($\Gamma \ll \delta$) was discussed above. Now we shall investigate the opposite limiting case, when $\Gamma \gg \sqrt{\sigma'_2}$, i.e., the broadening caused by the dependence of δE_n on atomic configuration is much smaller than the natural width. In this case we can make an expansion in (14) (or in the analogous expression for nonideal solutions) in powers of α and keep only the leading terms in the expansion. Then the characteristics of the spectrum can be expressed in terms of the same constants as for the case of $\Gamma \ll \delta$, if we note that

$$\sum_{\dots p_i \dots} A_p \Big[\sum_i (p_i - cz_i) \alpha_i \Big]^m = \sigma_m.$$

As a result we find that the frequency ω_m corresponding to the maximum of the spectral curve is given by the following formula, which is valid for both nonideal and ideal solutions:

$$\omega_m = \alpha^0 + \sigma'_1 - 8\sigma'_3/\Gamma^2. \tag{15}$$

Thus the dependence of ω_m on the order parameters for large values of Γ is found to be the same (neglecting higher order terms) as that found above for the average frequency when Γ is small.

We get different corrections ϵ to the width $\Gamma + \epsilon$ of the spectral curve for $\sigma'_1 = 0$ if we define it as the integral width or as the width at half maximum. This correction is expressible in terms of the second moment, and is equal to

$$\varepsilon = 4\sigma_{0}^{\prime}/\Gamma,$$
 (16)

in the first case, and to $\epsilon = 6\sigma'_2/\Gamma$ in the second. From (8) and (16) we see that for large Γ the width depends linearly on c(1-c) and not on $\sqrt{c(1-c)}$, as it does for small Γ . In contrast to the situation for small Γ , where this type of broadening is proportional to $(m_A - m_B)/m$, for large Γ the correction ϵ is proportional to $(m_A - m_B)^2/m^2$, and is unimportant when the relative mass difference is small. The dependence of the maximum intensity $\sigma_m(q, \omega)$ on the constants α is determined by the factor $(1 - \epsilon/\Gamma)$. The asymmetry index of the curve is expressed in terms of the third moment, and is equal to

$$(\omega_{+1/2} - \omega_{-1/2}) / \Gamma = 8 \sigma'_{0} / \Gamma^{3}.$$
 (17)

As for the case of small Γ , the asymmetry vanishes in the ideal solution when $c = \frac{1}{2}$. At the same time the asymmetry index in this case is ~ $(\Gamma/\delta)^3$ times smaller than for small Γ .

As already mentioned, the integral intensity of the line is determined by the average Debye factor $\langle D \rangle = \exp[-M_A(q)]$. We know that in ideal cubic crystals, in the harmonic approximation, MA is proportional to q^2 . But in solid solutions, according to ^[7], MA ~ q^2 only for small q. For large q the Debye factor is a more complicated function of q. In particular this has the consequence that even in cubic crystals MA depends not only on the magnitude but also on the direction of the vector q. Thus if the nuclei emit high energy photons (large q) one should observe a dependence of the emission (or absorption) intensity on the orientation of the emission direction relative to the axes of a cubic single crystal.

It has already been pointed out (cf., for example, ^[8]) that the intensity of the recoilless radiation can be increased by increasing the Debye factor, by introducing the radiating atom as an impurity in a crystal consisting of atoms with large masses. We have given an estimate of this effect.^[7] Here we mention only that at high temperatures, when the classical approximation is applicable, M_A does not depend at all on the masses of the atoms of the solution, and M_A can be reduced only by increasing the atomic interaction constants.

When we go over from ideal crystals to solid solutions, the distribution in intensity of the onephonon and multiphonon emission also changes. In particular, the singularities in the distribution function of the vibration frequencies and the singularities in the frequency dependence of the probability for one-phonon emission, which must occur in ideal crystals, are smeared out in solid solutions (cf. ^[5]).

We have here treated the broadening of the Mössbauer line associated with the dependence of

the change in vibrational energy δE_n on the atomic configuration. In a solid solution the difference in energy between the excited and ground states of the nucleus may also depend on the atomic configuration for other reasons, for example as a result of nuclear isomeric shift or magnetic shift of nuclear levels in a ferromagnet. In many cases these level shifts, in some approximation, depend additively on the nature of the surrounding atoms, i.e., they depend linearly on the numbers c_S in a formula of the type of (4). It is obvious that in these cases the spectral distribution of the Mössbauer line is again given by the above formulas. The only difference is that now the constants α_{s} which appear in these formulas have a different physical significance.

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