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RELAXATION NARROWING OF MÖSSBAUER GAMMA RAYS*

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Time-delayed coincidence measurements on Mössbauer gamma rays have demonstrated changes in resonance line shapes, including broadening and narrowing to less than natural linewidths.[1,2] These changes, which were first analyzed in terms of classical radiation theory[2] and later quantum mechanically,[3] are due to the modulation of the normally exponential decay of the resonance emission by electronic gating of the detector circuits. We wish to point out in this Letter that there exists a class of naturally occurring relaxation phenomena which may cause similar effects for Mössbauer gamma rays due to atomic and solid-state effects.

We consider systems in which the emission of the resonance gamma ray is preceded by a relatively energetic nuclear event, such that the local environment is initially disturbed from equilibrium, and subsequently relaxes in a time comparable to the gamma-ray lifetime. The relaxation process causes a modulation of the normally exponential decay analogous to modulations caused by instrumental means. The class of such relaxation phenomena includes the excitation of localized lattice-vibrational modes, temporary changes in atomic force constants, higher charge states, and atomic states which produce appreciably different quadrupole splittings in the excited and equilibrium states. We will here discuss one example, the case of heated localized modes.

Dilute impurities in regular lattices have locally distorted vibrational spectra when the mass or force constant of the impurity atom differs from the host atoms, and for significantly lighter impurities or greater force constants, there is a localized vibrational mode which lies above the vibrational band of the host.[4] The relaxation time of the localized mode depends upon its separation from the band and its anharmonicity: Relaxation times are estimated to be as much as 10^4 periods of the highest frequencies in the band.[5-7] We consider a radiating Mössbauer atom vibrating in a long-lived localized mode of frequency Ω_L, which has been stimulated to a vibrational amplitude greater than the equilibrium value. The mean-squared displacement x^2 of the impurity averaged over a period of the localized mode is assumed to relax with a single relaxation time $1/\gamma$ according to

$$x^2-\langle x^2\rangle=[x_0{}^2-\langle x^2\rangle]e^{-\gamma t}, \tag{1}$$

where $x_0{}^2$ and $\langle x^2\rangle$ are the initial and thermally relaxed values. The theory of Lax and Waller[8] shows that the usual form of the dependence of the recoil-free fraction on the displacement of the atoms in thermal equilibrium,

$$\langle f\rangle=\exp(-\langle x^2\rangle/\lambda\!\!\!^{-2}),$$

is justified even in the presence of normal mode damping, provided that the relaxation time is sufficiently long, $\hbar\gamma\ll kT$, $\gamma\ll\Omega_L$. Hence, we can calculate the time dependence of the gamma-ray intensity $|E(t)|^2$ and the corresponding line shape $|E(\omega)|^2$ by taking explicit account of the relaxation given by Eq. (1) and the transient $f=\exp(-x^2/\lambda\!\!\!^{-2})$. Adapting the usual equa-

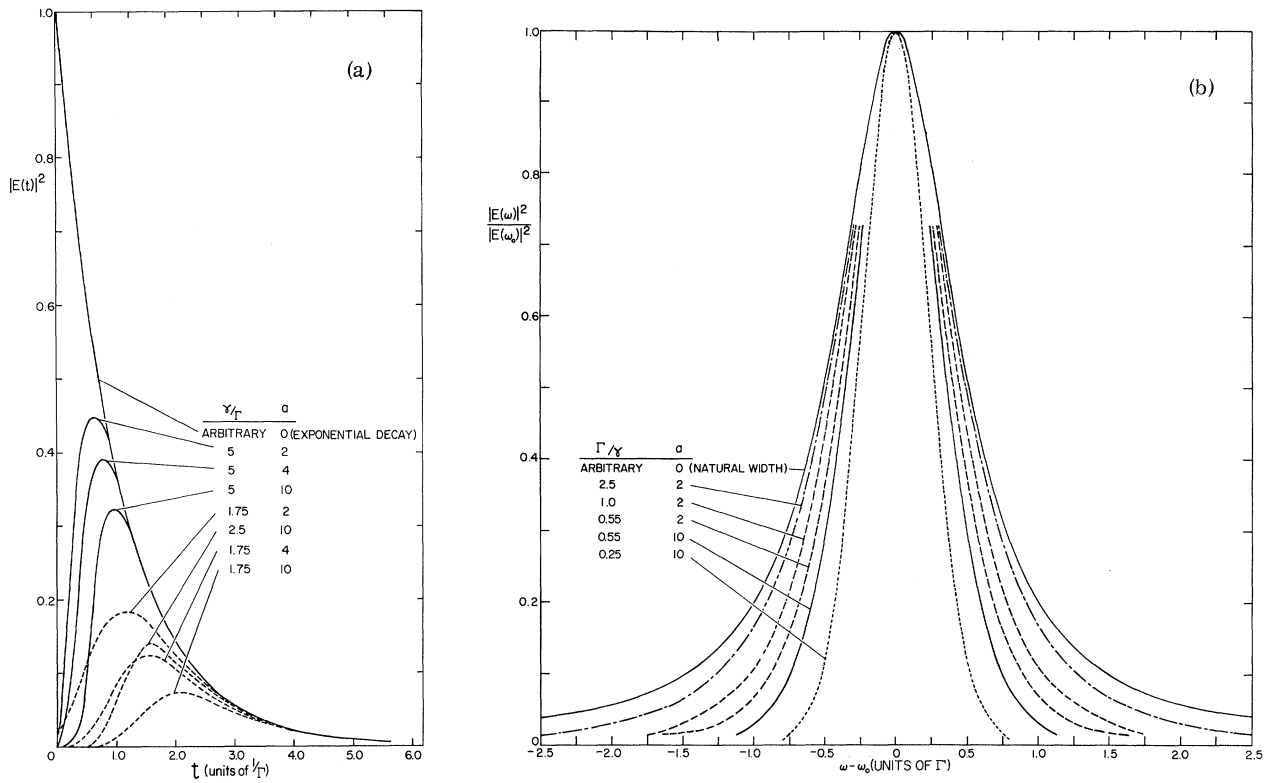

FIG. 1. Intensity of Mössbauer gamma rays of nuclear lifetime $1/\Gamma$ emitted from an impurity vibrating in a localized mode, for various values of the initial excitation a (see text) and localized mode lifetime $1/\gamma$. (a) Time dependence $|E(t)|^2$; (b) line shape $|E(\omega)|^2$.

tions[3,8] for $E(t)$ and $E(\omega)$, we obtain

$$E(t) = f^{1/2} e^{i\omega_0 t} e^{-\Gamma t/2}$$
$$= [\langle f \rangle]^{1/2} \exp(-ae^{-\gamma t}) e^{i\omega_0 t} e^{-\Gamma t/2}, \quad (2)$$
$$E(\omega) = [\langle f \rangle]^{1/2} \int_0^\infty \exp(-ae^{-\gamma t}) e^{i(\omega_0-\omega)t} \times e^{-\Gamma t/2} dt, \quad (3)$$

where ω_0 is the unshifted frequency and Γ is the natural width of the gamma ray, and $a = [x_0^2 - \langle x^2 \rangle]/2\lambda^2$. As illustrated in Fig. 1(a) for several values of a and Γ/γ, the relaxation modulates the normally exponential time dependence near $t = 0$, rounding the leading edge of the envelope. This causes a loss of high-frequency components in the line shape. In Fig. 1(b) we show several examples of normalized line shapes obtained by machine calculation from Eq. (3). It is seen that the relaxation produces non-Lorentzian narrowed lines, in which the principal change in shape is a depression of the wings of the lines. The narrowing is greater for both longer relaxation times and greater excitations a, and in Fig. 2 we show this dependence. It can be shown that the line tends toward a Lorentzian of zero width as $\gamma \to 0$ and $a \to \infty$ such that $a\gamma = \Gamma/2$.

The narrowing is accompanied by a substantial loss in over-all intensity of the Mössbauer radiation, equivalent to a reduction in the long-time-averaged $\bar{f}$ obtained in conventional experiments.[9] This reduction produces a fictitious temperature dependence of the apparent characteristic temperature θ_L' of the impurity mode, even if γ and a are not themselves temperature dependent. If γ and a are constant, $\bar{f}$ is a constant fraction ξ of $\langle f \rangle$ for all temperatures T of the host. This reduction, if attributed to a lowered θ_L of the localized mode, is a larger effect when $\langle f \rangle$ is near unity than for smaller values. In Fig. 3 we show the apparent variation of θ_L' with T for two sets of parameters. Although the characteristics illustrated are chosen to correspond to the emission of 14-keV gamma rays from Fe^{57}, this isotope may not be favorable for demonstrating the effect.

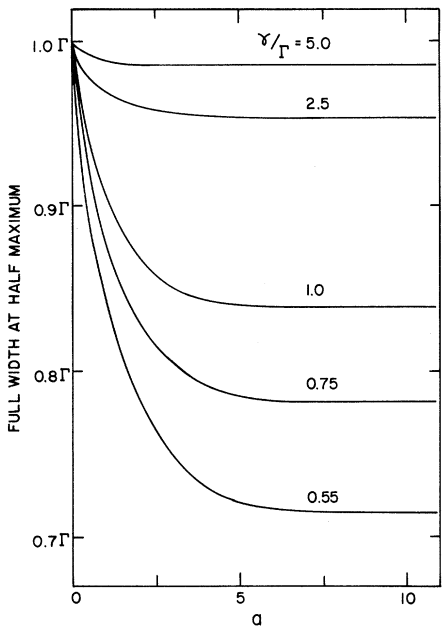

FIG. 2. Linewidths (full width at half-maximum) of relaxation-narrowed lines of natural width Γ as a function of excitation a and localized mode lifetime $1/\gamma$.

An attempt to detect the time dependence of f for Fe^{57} by direct measurement was not successful.[10] Experimental detection of relaxation may require gamma rays of shorter lifetimes, on the order of the estimated 10^{-10}- or 10^{-9}-sec lifetimes of localized modes. Nevertheless, it is noteworthy that some recent experimental studies[11-13] of $\bar{f}$ indicate an anomalous lowering of θ_L in Mössbauer sources at low temperatures, and these include studies of Fe^{57}.

The experimental results most suggestive of relaxation narrowing and associated reduction of θ seem to be the recent studies of K^{40} gamma rays, excited by the reactions $K^{39}(d, p)K^{40}$,[12] and $K^{39}(n,\gamma)K^{40}$.[13] These reactions impart kinetic energies to the K^{40} atoms sufficient to cause considerable radiation damage and local heating. The experimental linewidths were found to be 1.2 ± 0.35 mm/sec[12] and 1.1 ± 0.25 mm/sec,[13] compared to the natural width 1.2 ± 0.1 mm/sec corresponding to the electronically measured[14] half-life of 3.9 ± 0.35 nsec. The absence of any detectable isomer shifts in hosts of K, KCl, and KF could account for the lack of environmental broadening due to radiation damage, but it may be significant that the measurements gave mean values for the width equal to or slightly smaller than the electronic value. The KCl and KF sources[13] also showed an unusual temperature dependence of $\bar{f}$. The apparent θ was significantly lower than the value corresponding to the heat capacity, the decrease being significantly greater at 4° than at 78°K. This temperature dependence was not found in the KCl absorbers. To within the experimental uncertainty, we find that the ratio ξ of the experimental $\bar{f}$ to the $\langle f \rangle$ calculated according to the heat capacity θ is independent of temperature for both types of sources, which would correspond to temperature-independent relaxation parameters. On the basis of the $\bar{f}$ measurements, the relaxation time in both KCl and KF is 0.6 ± 0.4 of the mean life of the gamma ray: This time implies a linewidth 0.8Γ to 0.96Γ. Although the data are consistent with relaxation narrowing, it

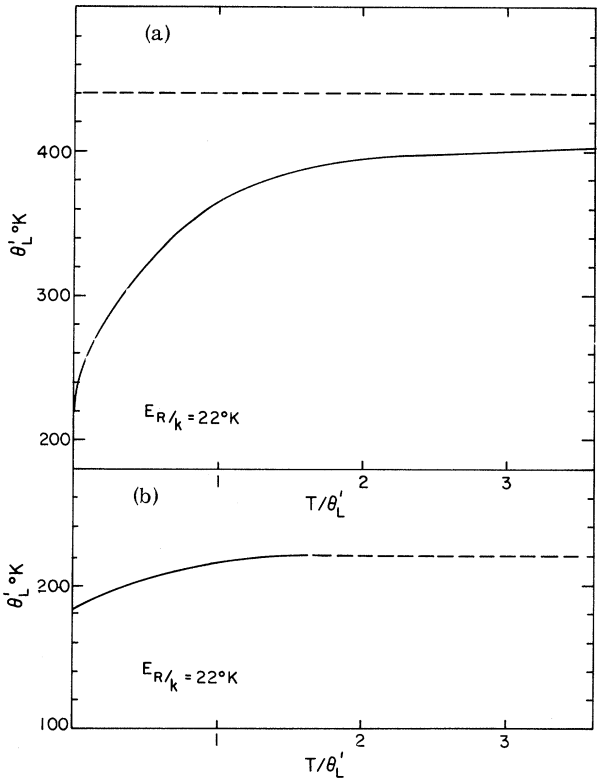

FIG. 3. Apparent characteristic temperatures θ_L' of impurities vibrating in localized modes of characteristic temperature θ_L, for two sets of parameters. θ_L' is obtained from an analysis of the decreased fraction $\bar{f}$ by attributing the decrease to a lowered localized mode temperature. (a) $\theta_L = 440$°K, $\langle f \rangle_{T=0} = 0.95$, $\xi = \bar{f}/\langle f \rangle = 0.95$; (b) $\theta_L = 220$°K, $\langle f \rangle_{T=0} = 0.90$, $\xi = 0.98$.

does not seem possible to identify the nature of the initial excitation with certainty. However, it is known that in such (n,γ) processes, a variety of short-lived and long-lived excited localized electronic states are produced. An atom in an excited electronic state can be expected to have a changed force constant K. If it changes to a significantly larger value, a localized mode can result, and narrowing can occur. Perhaps a more likely effect is a temporary reduction in K, which can cause effects similar to a hot localized mode, since x^2 varies inversely with K.

Additional features of the relaxation of a hot localized mode include the thermal shift and the emission and absorption of phonons such that there is zero net energy loss to the gamma ray during its emission.[8] A more detailed account of the relaxation of localized modes and other mechanisms which cause narrowing will be published elsewhere.

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EXTERNAL MODES OF VIBRATION OF SMALL POLYATOMIC IONS ISOLATED IN ALKALI HALIDES

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When a small polyatomic impurity ion is substitutionally isolated in an alkali-halide lattice, the frequencies of the normal modes of the free ion are perturbed by no more than a few percent. The vibration of the ion as a whole with respect to the supporting lattice, termed an external mode of vibration [Decius et al.[1]] and clearly representing the part played by the impurity in the perturbed lattice vibrations of the crystal, would, however, be expected to be strongly dependent on the supporting lattice. Although direct observation of these modes in the far infrared is hampered by the very strong host-lattice absorption, Sievers and Lytle[2] have observed some bands in KI doped with KNO_2, by working at low temperatures. Even at liquid-helium temperatures some of this region is masked by the host-lattice absorption, which broadens to obscure most of the region as the temperature rises. Combination of the external modes with strongly active internal modes can, however, be observed in the near infrared where the host lattice is transparent at all temperatures. This type of spectrum, which can be described as $\nu(\text{internal}) \pm \nu(\text{external})$, has been observed for several different ions, each isolated in a variety of alkali halides; and the pressure dependence of some of these spectra has been obtained.

As is indicated for this type of spectrum in the case of the NCO^- ion isolated in KBr in