Mössbauer effect, it is a relevant and a fair question to ask if this is the only way of obtaining the desired information, or even if it is the best way. A good, clever, informative experiment is hard to come by, either by theoreticians or by experimentalists, in any branch of science. The lattice dynamical applications of the Mössbauer effect are no exception. But, as it is often said in other contexts, "it's *got* to be hard to be good!"

ACKNOWLEDGMENT

I should like to thank Professor R. V. Pound for his helpful discussion on the temperature dependence of the isomeric and second-order Doppler shifts.

Optical Analogs of the Mössbauer Effect in Solids

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INTRODUCTION

After most new discoveries in physics there is a period of "digestion" as physicists learn to understand the new effect and in particular to relate it to their previous experience. This digestive process is most fruitful in giving a broader perspective and deeper insight in both the old field of research and the new one. Just such a process has occurred after the discovery by Mössbauer of recoil-free γ-ray transitions in solids. A number of people have been considering problems in solid state optical spectroscopy, a field active for over four decades, in terms of ideas developed in the last four years in the development of solid state γ-ray spectroscopy.[1] The first half of this paper will demonstrate that many of the underlying physical ideas in both fields are essentially the same. The remainder will illustrate this similarity by discussing a number of results of optical experiments in terms of their Mössbauer analogs.

THE ANALOGY

The Mössbauer effect has received a qualitative interpretation from several different points of view.[2] Although the effect is asserted by some to be purely quantum mechanical, a classical description is still instructive. In these terms one thinks of the nucleus held at rest as emitting a classical wave or γ ray of frequency ν_0. If the nucleus is in motion, as it will be in a solid, its "instantaneous frequency" as seen by an observer at rest will vary with time as a result of the Doppler effect and may be written schematically as

$$\nu_n(x,t) = \nu_0 + \frac{\nu_0}{c}\, v(x,t) - \frac{1}{2}\,\frac{\nu_0}{c^2}\, v^2(x,t) + \cdots . \tag{1a}$$

If the motion of the host crystal is described by the function $\mu(x,t)$ giving the displacement from equilibrium of the atom at position x and time t, the velocity of that atom is simply $\dot{\mu}(x,t)$ and Eq. (1a) may be rewritten

$$\nu_n(x,t) = \nu_0 + \frac{\nu_0}{c}\, \dot{\mu}(x,t) - \frac{1}{2}\,\frac{\nu_0}{c^2}\, [\dot{\mu}(x,t)]^2 + \cdots \tag{1b}$$

If the function $\exp\,[i \int^t \nu(x,t)\, dt]$ giving the complex amplitude of the classical γ ray is Fourier analyzed, the resultant spectrum has two characteristic features. The first feature is a sharp peak[3] at the frequency $\nu = \nu_0 - \langle \frac{1}{2}\,(\nu_0/c^2)[\dot{\mu}(x,t)]^2\rangle$; this is the recoilless emission line of γ-ray spectra or the carrier signal of radio frequency engineering. Its strength decreases as the depth of the Doppler-induced frequency modulation increases. The second feature is a continuous spectrum extending over a range of frequencies comparable with or larger than the typical frequencies describing the time variation of the displacement function $\mu(x,t)$. The detailed shape of this broad structure depends on the time dependence of $\mu(x,t)$, while its intensity increases as the mean amplitude of motion of the emitting nucleus increases. This structure is of course the multiphonon

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[1] The relationship between these two fields is either stated or implied in a number of papers. Some of these are: E. O. Kane, Phys. Rev. **119**, 40 (1960); E. D. Trifonov, Doklady Akad. Nauk. SSSR. **147**, 826 (1962) [English transl.: Soviet Phys.—Doklady **7**, 1105 (1963)]; R. Englman and P. Levi, J. Math. Phys. **4**, 105 (1963); See also reference 10. K. K. Rebane and V. V. Khizhnyakov, Optika and Spektroskopiia **14**, 491 (1963) [English transl.; Optics and Spectroscopy **14**, 262 (1963)].

[2] See H. Frauenfelder, *The Mössbauer Effect* (W. A. Benjamin, Inc., New York, 1962) and reprints contained therein.

[3] This peak is strictly a delta function only if the second-order Doppler shift is neglected and if the displacement function, $\mu(x,t)$, has a finite mean square. This second condition is satisfied for a three-dimensional solid in which diffusion is neglected, but not for liquids or one- or two-dimensional "model solids."

structure of the γ-ray spectrum, or the sideband signals of radio engineering.

A closely similar picture describes the emission of light when an electron makes a transition between states of an ion or structural defect in a crystal. In the electronic case the transition energy is strongly influenced by the positions of atoms or ions near the excited ion or defect, and the important coupling to the motion in the crystal is through the relative displacements of neighboring atoms, not through the velocity of the emitting ion.[4] It is convenient for illustration to assume a continuum model and let the energy shift be simply a function of the local strain at the defect $\epsilon(x,t)$, which in turn may be written as the gradient of the displacement function. One obtains

$$\begin{aligned}\nu_e(x,t) &= \nu_0 + \alpha\epsilon(x,t) + \beta\epsilon^2(x,t) + \cdots \\ &= \nu_0 + \alpha\nabla\mu(x,t) + \beta[\nabla\mu(x,t)]^2 + \cdots . \qquad (2)\end{aligned}$$

Except for the replacement of the time derivative in Eq. (1) by a space derivative in Eq. (2), the two equations are formally the same. The frequency spectrum will then be similar and, one expects to see a close parallel between the two types of systems.

In a very crude approximation the formal analogy may be extended by expressing the displacement function in terms of phonon coordinates. Using the continuum approximation above and adding the Debye assumption, $\omega = ck$, the frequency dependence of the coupling to the phonons is the same for both problems. Although strictly valid only for phonons at long wavelength, these assumptions probably give reasonable values for the coupling to short wavelength phonons for localized defects but are certainly not appropriate for defects, such as impurities in semiconductors, with electron orbits large compared with the lattice parameter.

Figure 1 illustrates the basic analogy in rather different terms. In the diagrams illustrating the nuclear transition, the small arrows indicate the zero point momenta of the atoms, the large arrow the momentum recoil of the emitting nucleus. In the electronic transition the heavy dots signify the equilibrium positions of the atoms. Note particularly that these equilibrium positions are different depending on whether the electron is in its excited or ground state. This displacement is a direct consequence of the coupling between the electron and its surroundings and is proportional to the square of the coupling coefficient α of Eq. (2). The shaded circles give the actual positions of the atoms, the shading to indicate the uncertainty associated with the zero point displacements of the atoms. The electron transition is considered to occur too fast for there to be appreciable atomic motion between the upper and lower pictures.

The nuclear recoilless emission is described as follows. After emission of the γ-ray photon, the emitting nucleus has a momentum in excess of its typical zero point momentum, or a momentum recoil, and associated with this momentum, a kinetic energy of recoil. Classically, one expects this recoil kinetic energy to be dissipated as heat in the crystal, but quantum mechanically there is a finite probability that the system be in its ground vibrational state after the emission. This probability of recoilless emission is obtained by squaring the projection of the state indicated schematically in the bottom of Fig. 1 onto the ground state of the crystal. This projection will be appreciable if the recoil momentum is comparable or small compared with the zero point momentum of the nucleus.

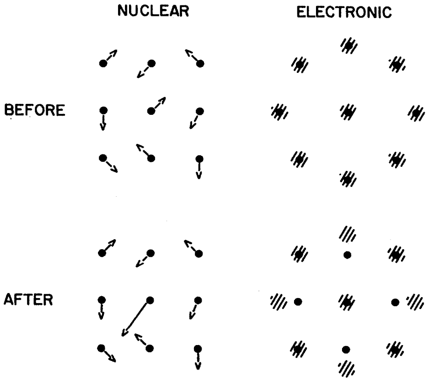

FIG. 1. A schematic illustration of the recoil analogy.

The paragraph above may be compared with the following description of the electron transition. After emission of the optical photon, the nuclei near the electron are displaced from their new equilibrium position, or have a "displacement recoil," and associated with this displacement, a potential energy of recoil. Classically, one expects this recoil potential energy to be dissipated as heat in the crystal, but quantum mechanically there is a finite probability that the system be in its ground vibrational state after the emission. This probability of recoilless emission is obtained by squaring the projection of the

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[4] There is, of course, a Doppler coupling to the lattice motion but this is typically very small compared to the strain coupling.

state indicated schematically in the bottom of Fig. 1 onto the ground state of the crystal. This projection will be appreciable if the recoil displacement is comparable or small compared with the zero point displacements of the nuclei.

The analogy is clear from a comparison of the two descriptions and may be shown explicitly by a simple translation of the above paragraphs into a suitable quantum mechanical formalism.[1]

The analogy might finally be expressed very simply in a yet different language, namely, that of molecular spectroscopy. If the crystal is considered to be a giant molecule and the γ-ray or optical spectrum is described in the language of band spectra, the Mössbauer line and its optical analog, when observed at $T = 0°\mathrm{K}$, are simply the zero–zero transition of the band spectrum. In the solid all higher order bands or lines typically merge into a continuum and the spectrum is characterized in both nuclear and electronic systems by a sharp zero–zero transition and a continuous single and multiphonon spectrum.

OPTICAL EXPERIMENTS

Having noted the similarity in principle between the γ-ray and optical spectra, one wonders whether this relationship is seen in experiment. A number of optical results are discussed below in terms familiar to the Mössbauer spectroscopists in order to illustrate the close connection.

The most critical parameter in a Mössbauer experiment is the recoilless fraction or f value of a particular host–nucleus system. This parameter is also important in the optical experiment in that it determines the qualitative behavior of the spectrum, not simply whether the transition is observed or not. Large f values are frequently observed, 0.95 being appropriate to the R lines or laser transitions in ruby and to some impurity transitions in semiconductors. In such instances, one typically observes only the sharp zero–phonon transition, the continuous or multiphonon structure being lost in the noise or ignored. At the other extreme are the so-called broad band spectra typified by the F-center absorption which in KCl has an f value of 10^{-10}. In these cases one observes only the multiphonon structure. The natural classification of optical lines into "broad" and "narrow" lines, with characteristically different dependences of width upon temperature, results from the simple experimental fact that one is usually observing either the zero–phonon transition or the multiphonon continuum but rarely both.

Fortunately, there are also systems in which the f value is appropriate to the observation of both the zero-phonon line and the multiphonon structure.[5] Figure 2 compares a theoretical spectrum computed by Visscher[6] with experimental results first obtained by Delbecq and Pringsheim[7] for the optical absorption of the R-center in LiF. Recognizing the difference in coupling strength for the two problems, the figure gives convincing evidence that the theory developed in understanding γ-ray spectra is pertinent in discussions of optical spectra.

Figure 2 is appropriate to measurements near absolute zero. As the sample temperature is increased, the thermal motion of the atoms increases the mean square velocities and strains in the crystal. This motion then results in an increase in the relative intensities of the multiphonon structure and a loss of intensity in the zero-phonon line. Figure 3 shows the experimental temperature induced variation of the zero-phonon intensity of some optical transitions and a fitted theoretical curve based on the appropriate generalization of the theory of the Mössbauer effect.[8] Again the γ-ray theory appears applicable to the optical problem.

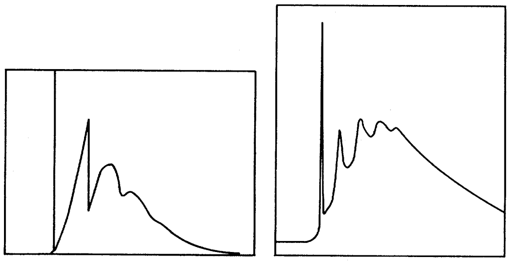
(a) THEORY- $R/k\Theta = 1.3$ (b) EXPERIMENT - $R/k\Theta = 2.6$

FIG. 2. (a) Calculation by Visscher of the γ-ray spectrum for a system with a ratio of momentum recoil energy to Debye energy of 1.3 (from Ref. 6). (b) Observation of electronic spectrum of R-center in LiF with a ratio of displacement recoil energy to Debye energy of 2.6 (from Ref. 8).

The f value at absolute zero and its temperature dependence, as well as the spectral shape of the multiphonon structure, are all derived in a first approximation from only the linear coupling to the lattice modes. There are also important physical conse-

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[5] A few examples are given in: R. W. Ditchburn, E. W. K. Mitchell, E. J. S. Paige, J. F. Custers, H. B. Dyer, and C. D. Clark, *Defects in Crystalline Solids* (The Physical Society, London, 1954), p. 92; M. H. L. Pryce and W. A. Runciman, Discussions Faraday Soc. **26**, 35 (1958); D. S. McClure, in *Solid State Physics* (Academic Press Inc., New York, 1959), Vol. 9, p. 488; R. E. Dietz, D. G. Thomas, and J. J. Hopfield, Phys. Rev. Letters **8**, 391 (1962).

[6] W. M. Visscher, Ann. Phys. **9**, 194 (1960).

[7] C. J. Delbecq and P. Pringsheim, J. Chem. Phys. **21**, 794 (1953).

[8] D. B. Fitchen, R. H. Silsbee, T. A. Fulton, and E. L. Wolf, Phys. Rev. Letters **11**, 275 (1963).

quences of the quadratic term, the most dramatic being the temperature dependence of the line shift or the Josephson shift of the Mössbauer line. As noted in the earlier qualitative discussion, the zero phonon line occurs at the frequency

$$\langle \nu(t) \rangle = \nu_0 - \tfrac{1}{2}\,(\nu_0/c^2)\langle \nu(t)^2 \rangle \qquad (3)$$

and is shifted from the frequency ν_0 by an amount proportional to the mean square velocity of the nucleus. In a monatomic crystal the total kinetic energy of the crystal will be proportional to this mean square velocity and if the system is harmonic so will the potential energy and hence the total energy. A similar argument applies to the electronic case where the shift is proportional to the mean square local strain. Thus one predicts a thermal shift directly proportional to the energy content of the crystal. Figure 4 shows a test[9] of this argument for an optical transition of Cr^{3+} in MgO. The remarkably good agreement is actually surprising since in the electronic case the result depends on questionable assumptions concerning the coupling to the short wavelength phonons. Certainly this relation would not be expected to hold for semiconductor systems where the coupling to these phonons would be much weaker than implied by the simple expression Eq. (2).

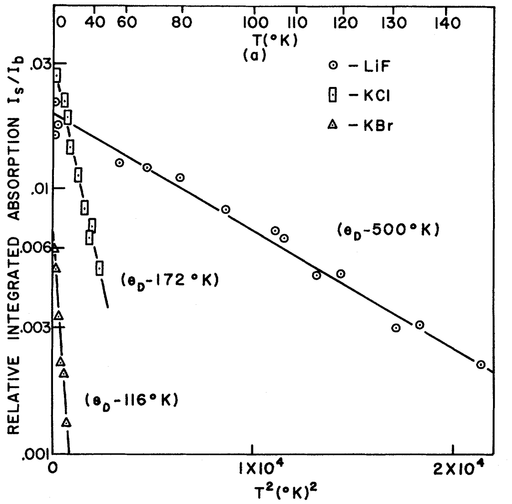

FIG. 3. Temperature dependence of the zero-phonon line intensity. The points give the relative integrated intensity of the zero-phonon line of the R_2 band in LiF, KCl, and KBr. The straight lines are the predictions of the Mössbauer theory with the Θ_D values indicated (from Ref. 8).

The shift indicated by Eq. (3) also contributes to the chemical shift of the Mössbauer line at absolute zero since the mean square zero point velocity of the nucleus will depend on the chemical environment of the nucleus. In the electronic case, for systems with the same chemical but different isotopic environment, the amplitude of the zero point motion and hence of the zero point strain will similarly depend on the masses of the nearby nuclei. This gives an isotope shift in the optical case which has been studied experimentally in ruby by Schawlow.[10]

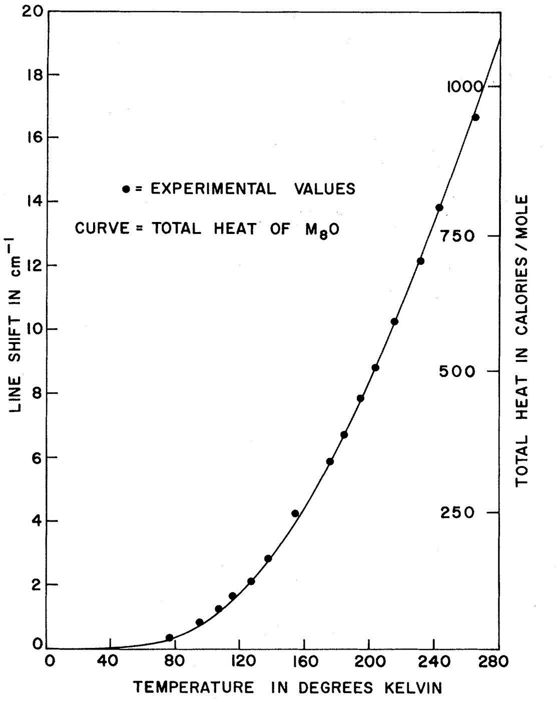

FIG. 4. A comparison of the thermal shift of a Cr^{3+} line in MgO with the total heat content of the crystal with the vertical scale adjusted for the best fit (from Ref. 9).

The quadratic term of Eq. (1) also gives broadening of the Mössbauer line.[11] After expansion in phonon coordinates this term, because it is quadratic in $\mu(x,t)$, may be seen to couple the γ-ray transition to pairs of phonon modes. Thus, during the transition, there can be an inelastic scattering of the phonons in which the total number of phonons is conserved but in which small amounts of energy may be given to or received from the lattice vibrations. The resulting width for the Mössbauer problem is much less than the natural width, but for many optical lines this is the major source of the temperature dependence of the linewidth. McCumber and

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[9] G. F. Imbusch, W. M. Yen, A. L. Schawlow, D. E. McCumber, and M. D. Sturge, Phys. Rev. (to be published).

[10] A. L. Schawlow, in *Advances in Quantum Electronics* (Columbia University Press, New York, 1961), p. 50.

[11] R. H. Silsbee, Phys. Rev. **128**, 1726 (1962).

Sturge[12] have shown that this mechanism gives a semiquantitative understanding of the temperature dependence of the line width of the ruby R lines. Thus an effect immeasurably small in the γ-ray problem becomes easy to observe in the optical analog.

APPLICATIONS

These experimental results were chosen to emphasize the qualitative similarities between the γ-ray and optical spectra of solids. The strong analogy raises the question of which technique is the more appropriate for the study of any specific problem. For almost all problems the choice is dictated specifically by the problem at hand. Optical absorption does not seem an attractive technique for the study of the mean square velocities of the surface atoms on crystals nor does it seem likely that the properties of lasers will receive much experimental study in γ-ray systems. There are problems, however, where the distinction is not so clear and two such examples are discussed below.

Much of the early interest in the Mössbauer effect was in the application of the effect to laboratory tests of relativity which were feasible as a consequence of the extraordinarily high Q values of this resonance, of the order of 10^{12} for Fe^{57}. In principle, the limiting Q's of the optical resonances are again simply the product of the state lifetime and the transition frequency and for many forbidden optical transitions Q's of the order of 10^{12} or higher are in principle attainable. In practice, systems are exceedingly far from this theoretical limit, the practical limit in most instances being determined by random residual crystal strains due various crystal imperfections. The Q of the ruby R line in a carefully prepared crystal, for instance, is only the order of 10^5.[9] Although the investigation of other optical systems and improvements in the techniques of crystal growth will certainly result in lines with much higher Q's than 10^5, it is unlikely that optical transitions will compete seriously with γ-ray transitions in the field of high-Q experiments.

Another area of potential application of the Mössbauer effect is in the study of lattice dynamics and in particular of localized modes. The technique suffers two disadvantages here. First, very high source velocities are required to obtain a sufficient Doppler shift to scan the frequency range of interest. Second, the method suffers from an excessively high resolution and the search for a localized mode becomes exceedingly difficult if there is appreciable lifetime broadening of the localized mode.

The optical technique, though it gives less information about the localized mode, is much more feasible experimentally. In a sense, localized modes have been observed as vibrational sidebands on electronic transitions in solids for some time.[13] These modes, however, are typically closely related to vibrational modes of the molecules, which constitute the solid in question and are not of the type of current interest to theoreticians, resulting from mass defects in the crystal.

Recently, however, the optical absorption has been directly measured for the localized mode produced by substitution of a hydrogen ion for a halide ion in the alkali halides.[14] This absorption, which is now a vibrational analog of the Mössbauer transition, is the strong line shown in Fig. 5. Note that there are also weak sidebands separated from the main absorption dip by about 40 cm^{-1}. It is not clear whether these sidebands represent one phonon emission to and absorption from the transverse acoustic continuum modes of the host crystal, or a "semi-localized" mode[15] which is strongly broadened by interaction with the continuum modes. In any case, the simplicity of this method of investigation of the normal mode spectrum of solids suggests that for many problems, it will be a more useful approach than the nuclear analog.

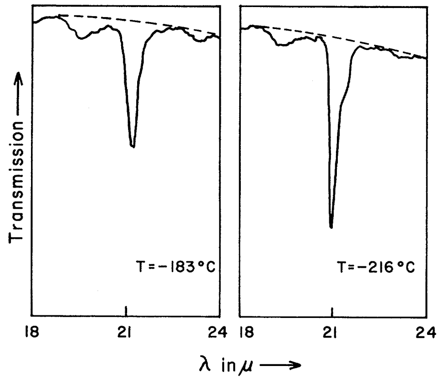

FIG. 5. The infrared transmission of RbCl:H$^-$ as a function of wavelength (from Ref. 14).

ACKNOWLEDGMENTS

This work was supported in part by the US Atomic Energy Commission and the Advanced Research Projects Agency.

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[12] D. E. McCumber and M. D. Sturge, J. Appl. Phys. 34, 1682 (1963).

[13] D. S. McClure, in *Solid State Physics* (Academic Press Inc., New York 1959), Vol. 9, p. 399.

[14] G. Schaefer, J. Phys. Chem. Solids 12, 233 (1960).

[15] R. Brout and W. M. Visscher, Phys. Rev. Letters 9, 54 (1962).