Debye-Waller Factor for the Cesium Ion in the Cesium Halides by Measurement of the Mössbauer Effect in Cs^{133}†

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(Received 10 June 1966)

The cesium halides have been studied in further Mössbauer measurements employing the 81-keV transition in Cs^{133} at 4.2°K. The values obtained for the recoilless fraction f_a are $100f_a = 1.59\pm0.06$ for CsF, 1.45 ± 0.07 for CsCl, 1.35 ± 0.07 for CsBr, and 0.94 ± 0.08 for CsI. The characteristic temperature Θ_M defined by $f_a = \exp(-3E_r/2k\Theta_M)$ has the value (in °K) 109 ± 1 for CsF, 106 ± 1 for CsCl, 104 ± 1 for CsBr, and 96 ± 2 for CsI. These results are qualitatively discussed in terms of the dispersion and polarization of the lattice modes. Both for CsF, which has the NaCl structure, and for CsI, which can be regarded as monatomic, values of the Debye temperature are deduced from the Mössbauer results and compared with available data.

INTRODUCTION

THE alkali halides have the simplest of the diatomic lattices for which a theoretical study of the dynamics can be made. The NaCl structure with its simple-cubic arrangement of ions has been studied extensively both theoretically and experimentally, but there has been comparatively little work on the alternative CsCl structure.

Apart from the determination of the actual dispersion relations through inelastic neutron scattering, there are many experimental quantities which depend on these relations and can be used in support, or otherwise, of theoretical predictions. Some of these quantities are, for example, the elastic constants, the specific heat, and the Debye-Waller factor. Reasonably accurate relations between some of these quantities can often be derived without the need for complete knowledge of the dispersion relations. In particular, the specific heat at 0°K can be related[1] to the elastic constants at 0°K since, in each case, only those modes near zero frequency are involved. Some knowledge of the complete dispersion relations is necessary, however, to relate either of these two quantities to the Debye-Waller factor; even at 0°K, the latter involves all the modes since it depends on the mean-square displacement of the ions in zero-point motion. In structures of the NaCl type, this problem has been considered by Kagan and Maslov[2] and we shall have occasion below to refer to their calculations.

Experimentally, the Debye-Waller factor can be found from the intensity of elastic scattering of either x-rays or neutrons, or from the fraction of recoilless transitions occurring in the emission or absorption of γ radiation. In the former method, absolute values of the scattered intensity are required, and for simple structures the presence of large extinction effects can affect these intensities to an extent that is often difficult to calculate. Further, the enforced neglect of the effects of structural disorder would ordinarily lead to an overestimate of the Debye-Waller factor. Neither of these disadvantages applies with the method using the Mössbauer effect, since it does not rely on interference effects but only on isolated emission or absorption events.

There have been many applications of the Mössbauer effect to this general problem. In particular, Hafemeister *et al.*[3] have determined the Debye-Waller factor at 80°K for the iodine ion in each of the alkali iodides. The experimental quantity that is measured is the recoilless fraction $f = \exp(-2W)$, where $2W$ is the Debye-Waller factor. The accuracy with which f can be measured does not usually depend very much on its magnitude, but more often on background corrections and the like, so that the accuracy of the determination of $2W$ is considerably improved if its value is large. For this reason it has been possible in the present work with the 81-keV transition in Cs^{133} to obtain more accurate values of $2W$ for the cesium halides than was possible for the alkali iodides. Further, the present measurements were made at 4.2°K, where virtually only the zero-point occupation of the phonon states is involved. Three of the cesium halides have the CsCl structure, and hence many of the present results are not comparable with the earlier work. However, there was one striking feature of the iodide results: The recoilless fraction changed but little from LiI to CsI. The same behavior is found here with the cesium halides.

EXPERIMENTAL

Basically, the experiment was of the standard Mössbauer type in which the transmission rate for the resonance radiation is recorded as a function of the velocity of the absorber.

† Work performed under the auspices of the U. S. Atomic Energy Commission.
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Source and Absorber

In earlier publications,[4] we have reported the observation of the Mössbauer effect with the 81-keV transition in Cs^{133}. The transition is between the $\frac{7}{2}^+$ first excited state and the $\frac{5}{2}^+$ ground state; the half-life of the transition is $(6.31\pm0.05)\times10^{-9}$ sec.[5]

The source for this transition was Ba^{133} which decays by electron capture with a half-life of 7.2 yr. A certain fraction of the decay events proceed by γ cascade through a level in Cs^{133} at 161 keV; the γ-ray spectrum thus includes an 80-keV line whose contribution[6] is 7% of the intensity of the unresolved line in this region.

The source material, as obtained from Oak Ridge, was in the form of $BaCl_2$. As we have previously reported,[4] considerable improvement in the effect results from the preparation of the compound $BaAl_4$. This preparation was carried out along the lines suggested by Alberti[7]; approximately 2 mg of active $BaCl_2$ (representing 2 mCi of Ba^{133}) was used as a flux for the reduction of about 10 mg of inactive BaO placed in a 1-g block of aluminum and heated in an inert atmosphere to about 1000°C for a few hours. Evidently there was sufficient exchange of Ba atoms between the flux and the alloy since after removal of the flux the alloy was found to contain something over half the original activity. The alloy was pressed into a disk of about 1-in. diameter. Two similar sources were prepared in this way and were used together for many of the measurements.

The powdered absorbers of the cesium halides, some of which are deliquescent, were mounted in Teflon containers and hermetically sealed. The thin absorbers were mixed with dried sea sand in order to achieve uniformity of thickness.

Velocity Spectrometer

The velocity spectrometer was the sinusoidal mechanical drive used in this laboratory in several previous investigations. The distance from source to counter remained fixed and the absorber was moved to scan the resonance. Both the source and the absorber were immersed in liquid helium, and the radiation emerged to an external scintillation counter through beryllium windows. An investigation was made of the background due to scattering from the cryostat walls. The background was then minimized by adjustment of the collimation. This was especially necessary when the thicker absorbers were being used.

EXPERIMENTAL RESULTS

Several authors, e.g., O'Connor,[8] have shown that the apparent total width Γ_{app} of the absorption dip in the velocity spectrum is given by

$$\Gamma_{app}=\Gamma_a+\Gamma_s+0.27\Gamma t, \quad (1)$$

where Γ_a and Γ_s are the widths of the absorber and source lines, respectively, and for various reasons are often greater than the natural width $\Gamma=0.267$ mm/sec determined from the lifetime[9] of the state; and t is the equivalent thickness of the absorber defined as $t=n\sigma_0 f_a$, where n is the number of atoms of the Mössbauer isotope per cc of the absorber, f_a is the recoilless fraction of the absorber, and σ_0 the cross section at resonance, is given by

$$\sigma_0=2\pi\lambda^2\frac{2I_e+1}{2I_g+1}\frac{1}{1+\alpha}.$$

α is the internal conversion coefficient. The K-shell conversion has been measured by Bergström *et al.*[10] as $\alpha_K=1.47\pm0.05$. This value is in excellent agreement with the calculations of Sliv and Band[11] who give $\alpha=\alpha_K+\alpha_{LI}+\alpha_{LII}=1.48+0.17+0.01=1.66$. From the latter, we have $\sigma_0=1.07\times10^{-19}$ cm^2.

Thus a series of measurements of Γ_{app} for a range of absorbers of different thickness can yield the values of t for these absorbers, and also the value of the sum $\Gamma_a+\Gamma_s$. Figure 1 shows the results of such measurements made with CsF absorbers. The straight line shown is a least-squares fit to the data. Its intercept at $t=0$ is $\Gamma_a+\Gamma_s=0.624$ mm/sec, to be compared with $2\Gamma=0.534$ mm/sec. With the value of σ_0 above, f_a could thus be determined from the slope of the line

$$f_a \text{ for CsF}=(1.59\pm0.06)\times10^{-2}.$$

This procedure could have been repeated for the other cesium halides, but an alternative method is available which involves the measurement of the velocity spectrum for only one value of the absorber thickness.

Several authors have shown that the area of the absorption line is independent of the width Γ_s of the

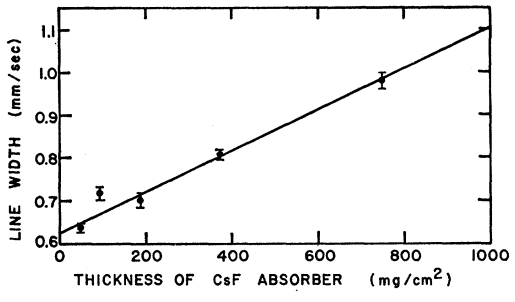

FIG. 1. The linewidth (full width at half-height) of the absorption spectra for several CsF absorbers of different thickness. The straight line is the least-squares fit to the experimental data.

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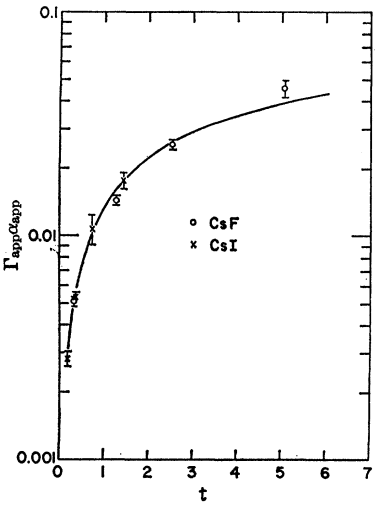

FIG. 2. Experimental values of $\Gamma_{app}\alpha_{app}$ for several absorbers of CsF and CsI. The t for CsF were found from the linewidths (Fig. 1). The solid curve is the function $f_s'\Gamma L(t)$ with $f_s'=0.062$. The t scale for the CsI absorbers has been adjusted for best fit to this function.

source line and that

$$\Gamma_{app}\alpha_{app}=f_s\Gamma_a L(t), \quad (2)$$

where, in the present case of lines that have almost the natural width, $L(t)$ is the function appropriate for Lorentzian spectra and has been tabulated by Lang,[9] and α_{app} is the fractional peak absorption corrected for background. We can rewrite (2) in the form

$$\Gamma_{app}\alpha_{app}=f_s'\Gamma L(t),$$

where $f_s'=f_s\Gamma_a/\Gamma$. Thus if f_s' is known, a single measurement of the area of the absorption dip can give the corresponding value of t and hence $f_a(=t/n\sigma_0)$.

The quantity f_s' could be determined for each of the measurements with the series of CsF absorbers, since the t values for these are known from the analysis through (1) of the apparent width of the lines. This gives the average value $f_s'=0.062\pm0.003$ for CsF. The plot of $\Gamma_{app}\alpha_{app}$ versus t is shown in Fig. 2, in which the solid curve is $f_s'\Gamma L(t)$ with $f_s=0.062$.

For the analysis of the other halide results it is necessary to assume only that Γ_a is constant; since all the crystals are cubic, diamagnetic, and of high purity, it is difficult to conceive of any reason for Γ_a to differ from Γ. For CsI, several absorbers of differing thickness were used. From the measured areas of the absorption dips, and with $f_s'=0.062$, the average value of the recoilless fraction of CsI was found to be $f_a=(9.4\pm0.8)\times10^{-3}$. The experimental results for $\Gamma_{app}\alpha_{app}$ are also shown in Fig. 2. with the abscissa scale determined by this value of f_a. Only one absorber thickness was used in the other measurements. The complete results for the recoilless fractions are shown in Table I.

All of the measured areas used in this analysis have had to be corrected for the background of radiations other than the 81-keV gamma ray which the channel is adjusted to select. The major part of the background derived from transitions of higher energy, and the correction varied considerably with changes in the absorber; it was usually between 20 and 80%. The 80-keV gamma ray is also part of this background, but is is a constant fraction and leads simply to a correction factor for the value of f_s' obtained above. Thus, if we assume that $\Gamma_a=\Gamma$, we have that for the $BaAl_4$ source

$$f_s=(6.6\pm0.6)\times10^{-2}.$$

DISCUSSION

For the discussion of the results above, it is useful to define a characteristic temperature Θ_M by the relation

$$f=\exp\left(-\frac{3}{2}\frac{E_r}{k\Theta_M}\right),$$

where $E_r=E_\gamma^2/2Mc^2$ is the recoil energy. For a Debye solid, Θ_M would be the Debye temperature. This relation is applicable only at 0°K, but for the cesium halides the modification at 4°K is negligible. The derived values of Θ_M appear also in Table I, and we note that there is comparatively little dependence on the halide ion. We have remarked above that a similar result was obtained with the alkali iodides.

Before we attempt a more detailed analysis, we can make a few qualitative remarks on this general behavior and its relation to specific-heat data. The Debye-Waller factor is $\langle(\mathbf{k}_\gamma\cdot\mathbf{u})^2\rangle$ where $\mathbf{k}_\gamma$ is the wave vector of the emitted or absorbed γ ray, and $\mathbf{u}$ is the ionic displacement.

The contribution to $\langle u^2\rangle$ from each of the phonon modes will be inversely proportional to the frequency ω of the mode. At 0°K the modes are equally populated and, since the frequency distribution increases roughly as ω^2, the major contribution to $\langle u^2\rangle$ will come from the region just inside the zone boundary. For a diatomic lattice with a significant energy gap at the zone boundary, the polarization of the modes is such that in the optical branch (particularly near the zone boundary) the heavier mass is virtually at rest, while in the acoustic branch it is the lighter mass which is at rest. Thus the optical branch makes practically no contribution to W if the heavier atom is the Mössbauer emitter; the major contribution arises from the motion of this atom in the potential of its virtually stationary lighter neighbors. In the series of alkali iodides or cesium halides, the mass of the emitter is necessarily constant. On

TABLE I. The recoilless fraction f_a of the cesium halides at 4°K, and the characteristic temperature Θ_M defined by $f_a=\exp(-3E_r/2k\Theta_M)$. The values of the Debye temperature Θ_D are derived from the 0°K elastic constants (Ref. 12).

Compound	f_a (%)	Θ_M (°K)	Θ_D (°K)
CsF	1.59±0.06	109±1	···
CsCl	1.45±0.07	106±1	···
CsBr	1.35±0.007	104±1	149
CsI	0.94±0.08	96±2	125

this picture, any variation in W could arise only through differences in the force constants. This picture loses validity as the masses approach equality and there will be some contribution to W from the optical branches. In these two series also, the noncentral force constants decrease as the lighter mass increases. Both of these effects result in a slight increase of W, and hence in a decreasing characteristic temperature Θ_M.

The low-temperature specific heat is characterized by quite a different portion of the phonon spectrum, and depends only on the slope of the dispersion relations near the center of the zone, i.e., near zero frequency. In the long-wavelength acoustic modes, both masses are moving more or less in phase and the Debye temperature will depend on the sum of the masses as well as on the noncentral force constants which determine the velocity of the low-frequency transverse wave. Thus Θ_D is expected to decrease more rapidly than Θ_M with increase in the mass of the lighter component.

For the CsI lattice in which the masses are nearly equal, Θ_M should be smaller than Θ_D since the frequencies that are important for $\langle u^2\rangle$ are lower because of dispersion than the Debye extrapolation from the slope near the origin. As the mass of the non-emitter decreases, the slope of the acoustic branch will increase and thereby raise Θ_D, whilst the frequency at the zone edge will remain unchanged (in so far as the force constants do not vary). The increased dispersion results from the introduction of the energy gap between the acoustic and the optical branches of the phonon spectrum.

Kagan and Maslov[2] have derived relations between $2W$ and Θ_D for monatomic and diatomic cubic lattices, and have made some numerical calculations for different values of the ratio ϵ of the masses and for the ratio $\xi=c_{11}/c_{44}$. The only application of this work has been to the alkali halide results of Hafemeister *et al.*[3] Upon correction of an arithmetical error, excellent agreement is found between the calculated and experimental recoillesss fractions of NaI and RbI, but the experimental value for LiI is considerably smaller than the theoretical prediction. Since the mass difference of NaI and LiI is small, we would expect Θ_M to show somewhat the same trend as Θ_D—they should both be determined predominantly by the relevant force constants. The value of Θ_D for LiI is considerably larger than that for NaI, in accord with the fact that c_{44} for LiI is almost twice as large as c_{44} for NaI. It is surprising, therefore, that the experimental values of Θ_M are about the same.

Since Kagan and Maslov made their calculations for the NaCl-type structure, we can apply their results to only one of the cesium halides, CsF. Unfortunately, there exist no measurements of the elastic constants of this crystal; but since the dependence of the calculations on ξ is slight, it is sufficient to use a value extrapolated from the complete data for the other alkali halides. The value of Θ_D derived in this way from the experimental result for Θ_M is $\Theta_D=154°$K for CsF.

Unfortunately there has been no specific-heat measurement made with CsF, and there are insufficient data on the elastic constants at 0°K to provide a useful extrapolation to CsF for the purpose of using the relation[1] between the low-temperature specific heat and the elastic constants. We may note, however, that $\Theta_D=164°$K for NaI at 0°K. NaI has almost the same masses and force constants as CsF, except that c_{44} is smaller for the fluoride; this should result in a slightly lower Debye temperature for the latter, in agreement with the prediction above.

Detailed consideration of the other halide results must await a theoretical treatment of the CsCl-type lattice. However, we can make some general comments concerning the result for CsI since this can be regarded as a monatomic crystal. At 0°K the Debye-Waller factor is given by

$$2W=(E_r/\hbar)\langle 1/\omega\rangle.$$

In the Debye approximation to the frequency spectrum, this reduces to

$$2W=\tfrac{3}{2}(E_r/k\Theta_M).$$

In CsI it is more realistic to assume an isotropic dispersion relation of the form

$$\omega=\frac{2}{\pi}\frac{k\Theta_D}{\hbar}\sin\tfrac{1}{2}\kappa a,$$

where the 0°K specific heat or the elastic constants define Θ_D, and hence the slope of the relation at the center of the zone. If we further assume a spherical zone, we have

$$2W=1.78E_r/k\Theta_D,$$

which gives $\Theta_D=1.25\Theta_M$. Thus we would predict a value of $\Theta_D\approx 120°$K. Vallin *et al.*[12] have measured the elastic constants of CsI and CsBr at helium temperature, and have used the method of Betts *et al.*[1] to obtain the values $\Theta_D=125°$K for CsI and $\Theta_D=149°$K for CsBr.

The agreement for CsI is very satisfactory considering the approximate nature of the model. The relative increase in Θ_D for CsBr illustrates the influence of the energy gap and the resultant increase in dispersion that appears when the two masses are not equal.

ACKNOWLEDGMENT

The authors wish to express their appreciation to J. Oyler for his aid in the laboratory.

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