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Observations of the Mössbauer Effect in Cs^{133}†

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In an extension of measurements on the Mössbauer effect of the 81-keV transition in Cs^{133} we have measured the isomer shifts of a variety of cesium chemicals, including the halides and the metal. The measurements were done in transmission at 4.2°K using a source whose nominal composition was $Ba^{133}Al_4$. The isomer shifts of the halides are shown to correlate linearly with the chemical shifts of their NMR frequencies. A fractional effect of $(1.86\pm0.26)\times10^{-4}$ was observed for the cesium metal, and the isomer shift with respect to $BaAl_4$ was -0.158 ± 0.057 mm/sec. When the latter is combined with the halogen shifts (which lead to an isomer shift of $\sim$0.3 mm/sec for Cs^+), it is found that the cesium decay product of Ba^{133} in $BaAl_4$ has the electron configuration $6s^2$. The existence of this species is supported by a plausibility argument in terms of the band structure of aluminum. The observed linewidth of the resonance in metallic cesium is 0.75 ± 0.18 mm/sec. In view of the source contribution, this is consistent with the natural linewidth. A spin-density-wave (SDW) ground state for Cs would lead to a hyperfine structure that was not observed. We conclude that for a linear SDW such as postulated for potassium by Overhauser, the linewidth indicates that the amplitude must be less than $\sim$1% or the relaxation time less than 6×10^{-10} sec. An area analysis of the absorption in the metal leads to a recoilless fraction $f_{Cs}=5.5\times10^{-5}$ and to the characteristic temperature $\Theta_M=49\pm1$°K. In comparison, the Debye temperature at 0°K is $\Theta_D(0)=40.5$°. From the shape of the function $\Theta_D(T)$ and the result $\Theta_M>\Theta_D(0)$, it is concluded that the phonon spectrum cuts off substantially higher than the frequency corresponding to $\Theta_D(0)$. A numerical calculation is made for the case of sodium where the spectrum is known and exhibits the predicted features. For this case a cancellation of two effects gives $\Theta_M=\Theta_D(0)$ within the error.

INTRODUCTION

In a previous communication[1] we reported the observation of the Mössbauer effect with the 81-keV transition in Cs^{133}; this transition has a half-life of 6.3×10^{-9} sec and occurs between the $\frac{5}{2}^+$ first excited state and the $\frac{7}{2}^+$ ground state. Since that time we have continued our work on the transition and have determined isomer shifts and recoil-free fractions for a series of substances, mainly cesium halides and cesium metal. A more complete discussion of the salts is deferred to a later publication; herein we report chiefly on results deduced from the Mössbauer effect in cesium metal.[2] In particular we are concerned with the calibration of isomer shifts, the measurement and interpretation of the Mössbauer temperature Θ_M, and the question of the possible existence of a spin-density-wave (SDW) state in cesium metal.

The source used in the present work was Ba^{133} alloyed with aluminum and inactive barium. It was prepared by reacting inactive BaO and active $BaCl_2$ with a large excess of aluminum in an argon atmosphere at about 1000°C. The inactive oxide is reduced by the aluminum and the barium forms an alloy into which the active barium enters by exchange. About half of the activity remained in the aluminum ingot after subsequent washing. It is presumed to be mainly in the form of the metallic compound $BaAl_4$,[3] although neighborhoods of nonstoichiometric, more aluminum-rich barium alloy may coexist with it. The experiment was done in transmission. The source was held stationary in a mechanical velocity spectrometer and the absorber moved with respect to it, both being at 4.2°K. The data were accumulated in a pulse-height analyzer operating in its "time" mode. The channel corresponding to zero velocity was determined periodically by use of the Mössbauer effect in Fe^{57}. The construction of the spectrometer is such that this furnishes a small correction ($\sim5\times10^{-3}$ mm/sec) to an otherwise absolute velocity scale. The data were treated by computer and fitted with single Lorentzians by use of the criterion of least squares with the fitting process furnishing error estimates. The observed absorption dips for the salts studied were typically about 1.5% and the position of the peak could be determined to somewhat less than 10^{-2} mm/sec in a run of about 20 h duration. Several runs were made for each salt and the positions averaged. For the cesium metal absorber an effect of only 1.9×10^{-4} was observed and it required three weeks of operation and $\sim3\times10^{10}$ counts to determine the position to 6×10^{-2} mm/sec. The cesium sample was prepared by distillation at high vacuum into a flat-walled Pyrex glass container which was then sealed off. The glass was kept below about 100°C during the distillation to avoid diffusion of metal into the wall. According to the manufacturer, the Cs concentration in Pyrex is less than 10^{-4}. If a cesium impurity amounting to about 1% of the total sample were present in the form of a compound precipitating in a separate phase and having

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[1] G. J. Perlow, A. J. F. Boyle, J. H. Marshall, and S. L. Ruby, Phys. Letters **17**, 219 (1965).

[2] A preliminary report has been given by G. J. Perlow, A. J. F. Boyle, and G. L. Montet, Bull. Am. Phys. Soc. **10**, 1112 (1965).

[3] M. Hansen, *The Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), p. 72.

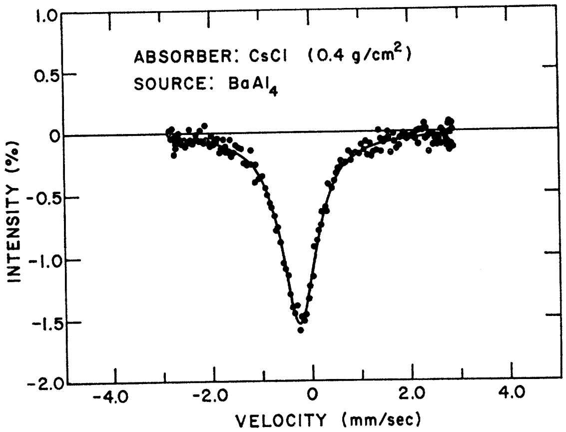

FIG. 1. Mössbauer effect in a typical salt.

the Debye-Waller factor of a typical cesium halide, its effect would be equal to the one observed. However, we believe that the concentration of such impurities in the sample did not exceed 0.01%.

RESULTS AND DISCUSSION OF THE ISOMER SHIFTS

A spectrum obtained with a representative halide (CsCl) is shown in Fig. 1, and that of metallic cesium in Fig. 2. The results of analysis of the metal spectrum appear in Table I. Table II lists all the shifts we have measured. The accuracy is relatively high for the halides and $CsMnF_3$. The other salts are listed for completeness. BaF_2 and $BaCl_2 \cdot 2H_2O$ were sources each emitting an unsplit line. They were measured with various absorbers, but are referred here to $BaAl_4$.

TABLE I. The resonance in cesium metal.

Fractional effect observed	$1.86 \pm 0.26 \times 10^{-4}$
Effect corrected for background	$4.1 \pm 0.6 \times 10^{-4}$
Observed width	0.75 ± 0.18 mm/sec
Observed shift	-0.158 ± 0.057 mm/sec
Shift corrected for zero-point motion	-0.164 ± 0.057 mm/sec
Goodness of fit: χ^2/degrees of freedom	1.05
Recoilless fraction f_{Cs} at 4.2°K	5.5×10^{-5}
Calculated Mössbauer temperature, Θ_M	49 ± 1°K

The samples have different Debye temperatures Θ_D and this results in a small difference in the second-order Doppler shift[4] due to different mean-square zero-point velocities. The shift in energy for a difference $\Delta\Theta_D$ and $T \ll \Theta_D$ is $9k\Delta\Theta_D/16\ Mc^2$. The correction increases the observed separation between $BaAl_4$ and Cs by 0.006 mm/sec and increases that between $BaAl_4$ and the salts by about 0.003 mm/sec. The corrections are included in the table.

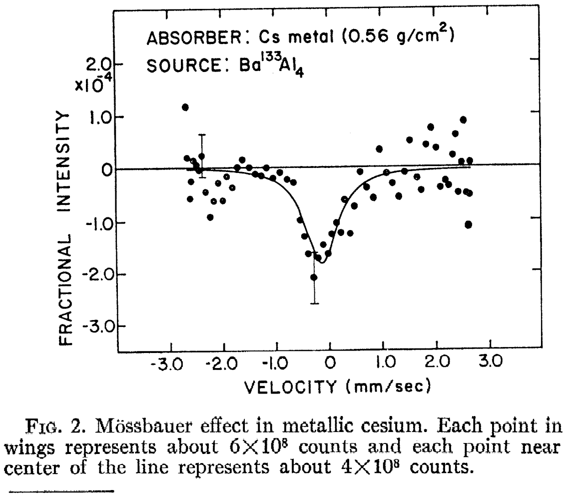

FIG. 2. Mössbauer effect in metallic cesium. Each point in the wings represents about 6×10^8 counts and each point near the center of the line represents about 4×10^8 counts.

The chemical shift of the cesium NMR frequency has also been measured in the cesium halides[5] and the values are included in Table II. In Fig. 3 we have plotted (curve *a*) these shifts against the corresponding isomer shifts. The data are more or less consistent with a straight line which intersects the isomer-shift axis at $S = -0.29$ mm/sec. Our most negative shifts ($CsMnF_3$ and Cs_2CO_3) are more negative by about 0.02 mm/sec.

The earliest theory of the chemical shift in the halides was developed by Yosida and Moriya,[6] who presumed that the bond between cesium ion and halide ion has a partially covalent character and that the shift arises from the paramagnetism of the unpaired *p* electrons in the outermost shell of the Cs atom; there is a corresponding chemical shift at the halide ion as a result of the fractional hole in its outer *p* shell. If we suppose that the transferred electron has a wave function of mixed character involving *s* and *p* orbitals with respective amplitudes A_s and A_p ($A_s^2 + A_p^2 = 1$), then the chemical shift will be proportional to $A_p^2 h_p$ and the isomer shift to $A_s^2 h_p$, where h_p is the fractional hole in the halogen ion closed shell. If we were further to assume that

TABLE II. Isomer shifts referred to a $Ba^{133}\ Al_4$ source. These have been corrected, where appropriate, for the effect of zero-point energy.

Substance	Isomer (mm/sec)	Chemical shift (NMR)[a] (10^{-4} mm/sec)
Cesium metal	-0.164 ± 0.057	
CsI	-0.247 ± 0.004	-2.52 ± 0.05
CsBr	-0.269 ± 0.004	-2.08 ± 0.05
CsCl	-0.269 ± 0.003	-1.63 ± 0.05
CsF	-0.278 ± 0.002	-0.9 ± 0.2
$CsMnF_3$	-0.313 ± 0.006	
CsN_3	-0.26 ± 0.01	
Cs_2CO_3	-0.32 ± 0.01	
$BaCl_2 \cdot H_2O$ (source)	-0.31 ± 0.02	
BaF_2 (source)	-0.28 ± 0.02	

[a] From Ref. 5.

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[4] R. V. Pound and G. A. Rebka, Jr., Phys. Rev. Letters 4, 274 (1960).

[5] H. S. Gutowsky and B. R. McGarvey, J. Chem. Phys. **21**, 1423 (1953).

[6] K. Yosida and T. Moriya, J. Phys. Soc. Japan **11**, 33 (1956).

A_s^2/A_p^2 is independent of the particular halide, the linear relation would be reasonable. It appears, however, that the covalency explanation is beset with serious quantitative difficulties in explaining either the chemical shifts or the isomer shifts. Indeed, we have been unable to understand the magnitude of our shifts by its use. Presumably an explanation is to be sought along the lines of the treatment of overlaps by Kondo and Yamashita[7] for the chemical shifts and more recently by Flygare and Hafemeister[8] for I^{129} isomer shifts. We propose to defer a more detailed discussion to subsequent work.

The isomer shift between a source and an absorber may be written

$$S = K\Delta|\psi(0)|^2 \Delta R/R,$$

where $\Delta|\psi(0)|^2$ is the difference in probability density (evaluated at the nucleus) of all the electrons of the two substances, $\Delta R/R$ is the fractional change of an appropriately defined nuclear charge radius between the ground state and the excited state, and K (which may be obtained, for example, from the article by Shirley[9]) is a constant depending on the nucleus. It is always assumed (perhaps without full justification) that the nuclear factors are unaffected by alteration of the chemical form and that only $|\psi(0)|^2$ changes. For the calibration of isomer shifts we shall refer all substances to atomic cesium and take the change in $|\psi(0)|^2$ between different substances to be equivalent to a change in the number of 6s electrons outside of a Cs^+ $(5p^6)$ core. In the hypothetical configuration $6s^n$ so defined, n is a function of S and may be greater than 2 if, for example, the atomic volume is reduced. With this definition, $n(S)$ is linear and we need only to determine two points on it. It is tempting to take the point S_0 for which $n=0$ at $CsMnF_3$ since it has the largest shift in the direction of diminishing n. Of course, it could in fact correspond to a loss of 5s density as a result of overlap with Mn^{++}. In that case, however, we might expect some transferred hyperfine structure since $CsMnF_3$ is antiferromagnetic with Néel point at 64°K.[10] No evidence for such structure was observed. Without detailed knowledge of the magnitudes, nothing further can be said. The precise location of $n=0$ is essential to an understanding of the shifts in the halides but not to the main purpose of this paper. We shall therefore merely note that $S_0 \approx -0.30$ mm/sec and indicate its uncertainty in Fig. 3 by using a dashed line.

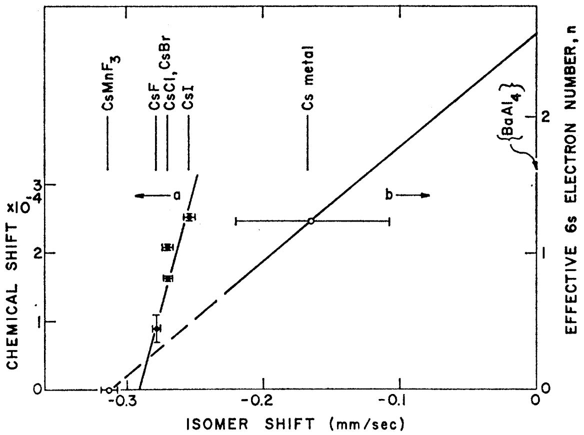

FIG. 3. (a) Chemical shift versus isomer shift for cesium halides. (b) Isomer shift versus effective 6*s* electron number *n*.

For the second calibration point, we have metallic cesium with $n \approx 1$. This number can be improved by considering the Knight shift of the NMR frequency which may be written[11]

$$\frac{\Delta\nu}{\nu} = \frac{8\pi}{3}\chi\langle|\psi_F(0)|^2\rangle_{\text{av}} = \frac{8\pi}{3}\chi\xi|\phi_A(0)|^2. \qquad (1)$$

Here $\Delta\nu/\nu$ is the fractional change in the NMR frequency between the metal and a diamagnetic salt (the chemical shift is much smaller), χ is the Pauli susceptibility per atom, and $\langle|\psi_F(0)|^2\rangle_{\text{av}}$ is the value (at the nucleus) of the probability density for a conduction electron at the Fermi surface, the angular parenthesis indicating an average over the Fermi surface. The factor

$$\xi \equiv \langle|\psi_F(0)|^2\rangle_{\text{av}}/|\phi_A(0)|^2$$

may be used in an alternative formulation to relate this density to the density $|\phi_A(0)|^2$ of a single valence electron in the free atom. The Fermi surface plays no special role in the isomer shift and one wishes instead to know about $\langle|\psi(0)|^2\rangle_{\text{av}}$, in which the average is now to be taken over all occupied states in the conduction bands. If the s character of the states at the Fermi surface were representative of the whole band, i.e., if $\langle|\psi_F(0)|^2\rangle_{\text{av}} = \langle|\psi(0)|^2\rangle_{\text{av}}$, then we could take $n=\xi$. The quantity ξ would be purely an experimental number deduced from the Knight shift and from atomic spectroscopy, if χ were known from experiment. It has appeared better to take χ from the calculations of Pines.[12] With the measured Knight shift and this value of χ, Benedek and Kushida[13] obtain $\xi = 1.13$ at room temperature, and by using their tabulated coefficients to make the temperature correction, we get $\xi = 1.23$ at liquid-helium temperature.

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[7] J. Kondo and J. Yamashita, J. Phys. Chem. Solids **10**, 245 (1959).

[8] W. H. Flygare and D. W. Hafemeister, J. Chem. Phys. **43**, 789 (1965).

[9] D. A. Shirley, Rev. Mod. Phys. **36**, 339 (1964).

[10] S. J. Pickart, H. A. Alperin, and R. Nathans, J. Phys. Radium **25**, 565 (1964).

[11] W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2. p. 93.

[12] D. Pines, Phys. Rev. **95**, 1090 (1954).

[13] G. B. Benedek and T. Kushida, J. Chem. Phys. Solids **5**, 241 (1958).

The band structure of cesium has been calculated in some detail by Ham.[14] The Fermi surface is reasonably spherical and does not contact the zone boundaries. The s character of the wave function at the Fermi surface is thus at least not greatly different from its value throughout the band. Without a detailed calculation, it appears most reasonable to take $n=\xi$. This along with S_0 supplies the necessary data for plot b of Fig. 3.

From plot b we observe that $n\approx 2.6$ for the source. What is especially interesting is that the source configuration corresponds roughly to $6s^2$, that is, to twice as many valence s electrons as in metallic cesium. We can attempt to make plausible the existence of the additional s character even though we cannot, in fact, claim to "explain" it. Following the decay of the barium, the resulting cesium is an exceedingly dilute impurity at a barium site in BaAl_n alloy, where n is 4 or greater. Soft x-ray spectra of aluminum in alloys containing up to 20% of magnesium show little change from the band structure of pure aluminum[15]; thus the relatively small addition of divalent barium is unlikely to make gross changes in the over-all band structure, and we shall take the host to be metallic aluminum. The conduction bands of aluminum contain three electrons: Two electrons fill the first zone and have largely s character; the remaining electron occupies regions of the 2nd and 3rd zone and has largely p character.[16]

In Cs metal we usually take the conduction band to contain one electron and describe the ion cores by Cs^+. If an impurity Cs^+ ion is introduced into the aluminum structure we have the problem of shielding the two extra charges of the Cs^+ ion; this is effected by a cluster of holes in the aluminum conduction band surrounding the impurity ion. The energy of these holes, however, is lower than that of some of the $5p$ electrons the Cs^+ ion; thus the holes can be filled leaving a core described approximately by Cs^{+++}, and a more or less complete conduction band.

As Daniel[17] has shown, the partial-wave character over the entire conduction band at the Cs ion is, in the absence of shielding, the same as that of the aluminum host, and thus an isomer shift corresponding to $6s^2$ is to be expected.[18] Although the effects of shielding are small there should be some modification to this conclusion from the fact that the pseudopotential for p electrons at the Cs ion will be deeper than that for s electrons; on the other hand, the loss of some $5p$ density will lead to a small increase in the s density at the Cs nucleus.

In Ref. 1 we deduced a tentative value $\delta R/R=2.3\times 10^{-4}$ for the fractional increase in nuclear radius of the excited state over that of the ground state. We assumed that $n=1$ for the decay product of BaAl_4 and $n=0$ for the ionic salts. With the aid of Fig. 2 and the equation

$$dS/dn=6.8\times 10^{-23}(\delta R/R)|\phi_A(0)|^2 \text{ in mm/sec} \quad (3)$$

with $|\phi_A(0)|^2=2.0\times 10^{25}\ \mathrm{cm}^{-3}$, we may recalculate and obtain $\delta R/R=8.9\times 10^{-5}$. The excited state has the larger radius.

SPIN-DENSITY WAVES

Overhauser[19] has postulated and given some evidence that the paramagnetic ground state of an electron gas can be unstable with respect to the formation of a spin-density wave (SDW). This is a type of magnetic ordering in the form of a static spatial distribution of spin polarization. In one simple form (a spiral SDW), the polarization has components $P_x=P_0\cos Qz$, $P_y=P_0\sin Qz$, $P_z=0$, with the SDW vector $\mathbf{Q}$ along the z axis. Linear spin-density waves of the type $\mathbf{P}=P_0\boldsymbol{\varepsilon}\cos\mathbf{Q}\cdot\mathbf{r}$ are also postulated. The polarization vector $\boldsymbol{\varepsilon}$ need have no special orientation with respect to $\mathbf{Q}$. The SDW in general is incommensurate with the lattice. The antiferromagnetism of chromium is cited as an example of a giant SDW structure. More recently, the results of optical-absorption measurements in potassium[20] have been explained[21] as due to a linear SDW state with $P_0=0.09$ Bohr magneton/atom. Because of their low electron density the alkali metals are considered to be especially likely to have SDW ground states. If this were the case in cesium metal, we should expect to observe a magnetic hyperfine structure characteristic of Zeeman transitions in an effective internal field H_{eff} such that

$$\mu H_{\mathrm{eff}}=aIJn|P|\,. \quad (4)$$

Here μ is the magnetic moment of the nuclear ground state, a is the hyperfine-interaction constant for a free atom in the atomic state J and nuclear ground state I, n is the effective $6s$ electron number previously defined, and $|P|$ is the magnitude of the polarization in Bohr magnetons/atom at the particular atomic site from which the gamma ray is emitted. For a spiral SDW in cesium metal, P would be the same at each site and a more or less sharp Zeeman pattern would be observed. For a linear SDW, because of the incommensurability, the internal field would vary from site to site and the pattern would be smeared.

The magnetic moment of the excited state, measured by precession of angular correlation, is $\mu_{\mathrm{exc}}=+3.1\pm 0.3$ nm.[22] The magnetic moment of the ground state is

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[14] F. S. Ham, Phys. Rev. **128**, 82 (1962); **128**, 2524 (1962).

[15] R. K. Dimond (private communication).

[16] V. Heine, Proc. Roy. Soc. (London) **A240**, 340 (1957); W. Harrison, Phys. Rev. **118**, 1182 (1960).

[17] E. Daniel, J. Phys. Chem. Solids **10**, 174 (1959).

[18] We wish to acknowledge receipt from P. Kienle of a communication which pointed out that this possibility existed, but for a different reason.

[19] A. W. Overhauser, Phys. Rev. **128**, 1437 (1962).

[20] M. H. El Naby, Z. Physik **174**, 269 (1963).

[21] A. W. Overhauser, Phys. Rev. Letters **13**, 190 (1964).

[22] E. Bodenstedt, H. J. Korner, and E. Matthias, Nucl. Phys. **11**, 584 (1959).

2.579 nm.[23] The pattern of 18 lines which result from an $M1$ γ-ray transition will extend over an energy range $\Delta E = 2(\mu_{\mathrm{exc}} - \mu_{\mathrm{gnd}})\ H_{\mathrm{eff}} = (1.0 \pm 0.6\mu_n) H_{\mathrm{eff}}$. The hyperfine-interaction constant in the state $I = \frac{7}{2}$, $J = \frac{1}{2}$ is 2298 Mc/sec. From this we find $H_{\mathrm{eff}}/P = 2.045 \times 10^6$G and

$$\Delta E/P = 6.4 \times 10^{-6}\,\mathrm{eV} = 24\,\mathrm{mm/sec}. \qquad (5)$$

The measured width of the cesium metal resonance (0.75±0.18 mm/sec) is actually consistent with the natural width since the $\mathrm{BaAl_4}$ has been shown to exhibit a minimum measurable width of 0.62 mm/sec.[24] If, however, we were to attribute the apparent broadening (0.13 mm/sec) to an SDW, we should have $P_0 \lesssim 0.006$ for a spiral SDW and $P_0 \lesssim 0.01$ for a linear SDW.

The spin-density wave described by Overhauser is a static distribution. Because of various interactions, however, we could think of it as relaxing—for example, by a translation parallel to **Q**. If the relaxation rate were rapid enough, one would measure only the natural linewidth. We may calculate the relaxation rate necessary to give the apparent broadening. By analogy with the theory of motional narrowing in nuclear magnetic resonance,[25] we may write (using frequency units)

$$\Delta\omega = \langle \Delta\omega_0^2 \rangle_{\mathrm{av}} \tau_c. \qquad (6)$$

Here $\Delta\omega$ is the increase in the linewidth of the source over the natural linewidth, τ_c is the correlation time for the relaxation process, and $\langle \Delta\omega_0^2 \rangle_{\mathrm{av}}$ is the second moment of the entire spectrum in the absence of the relaxation. From Eq. (5) we then get

$$\tau \lesssim 5 \times 10^{-12} P^{-2}\ \mathrm{sec}.$$

If the polarization were like that described for potassium, we should have $\tau \lesssim 6 \times 10^{-10}$ sec in order to observe a line as narrow as ours. This would be a very modest rate for a single spin but for a coupled system extending over some distance it might have to be considered quite rapid. In any case, we may say that if the ground state of cesium metal at 4.2°K is a spin-density-wave state, it is either of small amplitude or it could hardly be called static.

MÖSSBAUER TEMPERATURE AND THE PHONON SPECTRUM

The recoilless fraction of the source used here has been determined[24] to be $f_s = 0.066$. The recoilless fraction for the cesium metal absorber can then be determined from the area of the absorption dip with the result $f_{\mathrm{Cs}} = 5.5 \times 10^{-5}$. This value corresponds to a Mössbauer temperature $\Theta_M = 49 \pm 1$°K. The latter quantity is defined as the characteristic temperature of a fictitious Debye solid having the same Debye-Waller factor $2W$, i.e.,

$$f = e^{-2W} = \exp(-\tfrac{3}{2}(E_r/k\Theta_M)[1 + \phi(\Theta_M/T)]),$$

$$\phi(\Theta_M/T) = 4(T/\Theta_M)^2 \int_0^{\Theta_M/T} x\,dx/(e^x - 1), \qquad (7)$$

where E_r is the recoil energy of a free nucleus and $\phi(\Theta_M/T)$, the temperature-dependent part of the Debye-Waller factor, amounts to 0.048 in the present case. The error we have quoted for Θ_M is due to statistics. The chief source of systematic error is the possibility of contamination in the form of oxide or hydroxide formed by the gettering action of the vapor stream in the distillation process used for the preparation of the absorber. A contamination of 0.1% would result in an apparent raising of Θ_M by about 1°K. We believe the contamination to be considerably less. It must be pointed out that a cesium compound that remains in solution at 4.2°K is unlikely to have a serious effect on f_{Cs} except at much higher concentrations, nor is contamination by another alkali metal expected to be important.

In our experiment (in which $T \approx 0.1\Theta_M$), the quantity f is determined chiefly by the temperature-independent part of the Debye-Waller factor, i.e., by the zero-point motion of the lattice modes. If their frequency spectrum were indeed a Debye spectrum so that $N(\nu) = N_D(\nu) \propto \nu^2$, we should have $\Theta_M = \Theta_D$. Low-temperature specific-heat measurements give the Debye temperature at 0°K a value $\Theta_D(0) = 40.5°$.[26] The value of Θ_D dips to 36° at $T = 2$°K, rises to 45° at $T = 9$°K,[27] and thereafter remains roughly constant. The initial dip indicates that $N(\nu)$ at least initially rises with increasing frequency above the Debye spectrum $N_D(\nu)$ that corresponds to $\Theta_D(0)$. The Debye-Waller factor for $T \ll \Theta_D$ is given[28] by

$$2W = \frac{E_r}{h} \int_0^{\infty} N(\nu) \nu^{-1} d\nu; \qquad (8)$$

such a rise would, if maintained, make $2W$ larger than the value obtained by substituting $\Theta_D(0)$ for Θ_M in (7). That is, it would make $\Theta_M < \Theta_D(0)$. This would be the normal situation in a reasonably isotropic lattice and is accounted for by the dispersion of the lattice waves. Our contrary result, however, is in accord with the further behavior of the Θ_D value; the increase in Θ_D and our result $\Theta_M > \Theta_D(0)$ both indicate that over a significant part of the frequency spectrum, the density function must drop below $N_D(\nu)$ and hence must go to zero at some frequency higher than $k\Theta_D(0)/h$.

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[25] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, England, 1961), p. 426.

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[27] D. C. McCollum, Jr. and H. B. Silsbee, Phys. Rev. **127**, 119 (1962).

[28] A. J. F. Boyle and H. E. Hall, Rept. Progr. Phys. **25**, 475 (1962).

This conclusion could be tested immediately if the frequency spectrum of cesium were known. In its absence, we have examined the spectrum of metallic sodium which has been obtained by analysis[29] of neutron-scattering data. The sodium spectrum does indeed have both the features we describe, i.e., a higher frequency cutoff $[h\nu_{\max}\approx 1.2k\Theta_D(0)]$, and an initial rise above the Debye spectrum $N_D(\nu)$.[30] A numerical evaluation with the aid of Eq. (8) gives $\Theta_M=154°$ with an uncertainty of perhaps 5°K. Specific-heat measurements[31] give $\Theta_D(0)=156\pm 2°\text{K}$. We observe that $\Theta_M=\Theta_D(0)$ within the error. It is interesting that the two processes yield so nearly the same characteristic temperatures when analyzed in terms of a Debye solid despite the different average that is taken over the frequency spectrum. In this sense, it is perhaps also interesting that Θ_M and $\Theta_D(0)$ differ by relatively little for cesium, since a factor ~ 2 in their ratio can readily be obtained from a not-too-pathological set of phonon dispersion relations.

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Theory of Atom-Metal Interactions. I. Application of Quantum-Mechanical Collision Theory to Field-Ionization Processes*

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The principles of the field-ion microscope have been qualitatively well described by one-dimensional models in which the WKB approximation is used to calculate the probability of an atomic electron penetrating the potential barrier into the metal. It was concluded from such models that field ionization cannot occur once the atoms come closer to the tip than a certain critical distance. Recent experiments have shown that the ions are produced in a very narrow region of space just outside the critical distance, this region being called the ionization zone. The one-dimensional calculations give a value for the half-width of this zone which is about twice the experimental value. In the present treatment, the width of the ionization zone and a relative ionization probability have been calculated quantum-mechanically in a three-dimensional model. This is done by considering the process of field ionization as a rearrangement-type collision of an atom with a metal surface and applying the formalism of quantum-mechanical scattering theory. The calculated results are found to be in better agreement with experiment than previous one-dimensional theories.

I. INTRODUCTION

THE principles of the field-ion microscope (hereafter called FIM) have been qualitatively well described by the one-dimensional model proposed by Müller and others,[1,2] in which the WKB approximation of quantum theory is used to calculate the probability of an atomic electron penetrating the potential barrier into the metal. No three-dimensional quantum-mechanical calculation of the above transition probability had previously been made.

It was concluded from the one-dimensional model that field ionization cannot occur once the atoms come closer to the tip than a certain critical distance. This distance, determined by the matching of the Fermi energy of the metal with the atomic electron's energy level, varies with tip material and applied field and is well verified experimentally. Recent experiments by Tsong and Müller[2] on the energy distribution of ions produced in a FIM have shown that the ions are produced in a very narrow region of space just outside the critical distance, this region being called the ionization zone. The narrowness of the zone is indicated by the fact that the half-width of the energy-distribution curve of

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