one could presumably find a set of displacements which would account for the values of v and v' observed for each ion, the exercise seems hardly worthwhile.

The Mn^{4+} ion may be locally charge compensated by an Mg^{2+} ion in the nearest Al^{3+} site, which lies on the trigonal axis. If this is the case, the data show that v' is insensitive to the presence of the Mg^{2+} ion, reinforcing the argument that v' depends only on a long-range interaction.

To sum up, we have found that in Al_2O_3 the ground-state splitting of a $(3d)^3$ ion and the effect of stress upon it varies only slowly from ion to ion, and varies in the sense predicted by the point-charge model. The ^2E splitting, on the other hand, varies greatly from ion to ion, and the effect of stress varies even more dramatically. Interpreting these results in terms of Macfarlane's theory, we conclude that in Al_2O_3 v' depends primarily on long-range electrostatic interactions, whereas v depends on short-range interactions and may be sensitive to local rearrangements of the ions and possibly to local charge compensation. To our knowledge no microscopic theory[33] has so far been put forward which predicts this pronounced difference between v and v'.

ACKNOWLEDGMENTS

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[33] See, for instance, D. E. Rimmer and D. F. Johnston, Proc. Phys. Soc. (London) **89**, 953 (1966); R. Englman, J. Chem. Phys. **45**, 3862 (1966); and K. Zdansky, Phys. Rev. **159**, 201 (1967).

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Mössbauer Measurements with K^{40}†*

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This paper describes an investigation in which the 29.4-keV γ ray formed in the neutron capture reaction $K^{39}(n, \gamma)K^{40}$ was studied by use of the Mössbauer effect. Several potassium compounds were used as the neutron targets, i.e., as γ-ray sources for Mössbauer measurements. The results are: (a) All spectra show a single absorption line at $v=0$ whose width is no more than 1.3 times the minimum predicted from the lifetime; (b) the background and the recoilless fraction vary strongly from one case to another; and (c) the quadrupole splitting and isomer shifts are small if not zero. The recoilless fraction was measured as a function of temperature for a KF target. By fitting the results to curves based on a simple theory of diatomic solids, a value for the effective Debye temperature of potassium in these targets was obtained. In order to arrive at a value of $\delta\langle r^2\rangle/\langle r^2\rangle$ for the K^{40} nucleus, four careful center-shift measurements were carried out with K metal at 10°K and KF at 10, 55, and 80°K as targets, and KCl at 80°K as absorber. Comparison of these results with calculations of the thermal shifts based on our determinations of the effective Debye temperatures of the different targets shows that the measured line shifts are mainly due to thermal shifts. The accuracy of the measurements is sufficient to place an upper limit of $\delta\langle r^2\rangle/\langle r^2\rangle \leq 5\times10^{-4}$ for K^{40}.

I. INTRODUCTION

OF all nuclides with suitable properties for the Mössbauer effect, the one with lowest Z is K^{40}—but it does not have a radioactive parent. Two groups[1,2] have investigated nuclear reactions, one by (n, γ) reactions[1] and the other by (d, p),[2] as a means of forming a suitable number of excited K^{40} nuclei in an appropriate chemical or solid-state environment. The neutron-capture method proved to be the more useful one, and provided quantitative results. In particular, within the large experimental error, the result of Hafemeister and Shera,[1] using the (n, γ) reaction, showed no isomer shift between K and KF. This led to the conclusion that the fractional change of the expectation value of the squared nuclear charge radius is $\delta\langle r^2\rangle/\langle r^2\rangle < 80\times10^{-4}$.

According to Goldstein and Talmi,[3] the $f_{7/2}$ neutron

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§ This work was partially supported by the U. S. National Science Foundation (Grant No. NSF GK 871).

[1] D. W. Hafemeister and E. B. Shera, Phys. Rev. Letters **14**, 593 (1965).

[2] S. L. Ruby and R. E. Holland, Phys. Rev. Letters **14**, 591 (1965).

[3] S. Goldstein and I. Talmi, Phys. Rev. **102**, 589 (1956).

state and the $d_{3/2}$ hole state can couple together to form four levels whose angular momenta are 4^-, 3^-, 5^-, and 2^-. This study is concerned with the first two of these. Calculations on the binding energy[4] and the magnetic moment[5] of this nucleus have been made and fit the experimental results rather accurately. Since the coupling of the states involves only the angular parts of the wave function, this model leads to the conclusion that $\delta\langle r^2\rangle/\langle r^2\rangle$ for the K^{40} nucleus will be zero—in agreement with the initial experiments.

On the other hand, a simple calculation of the electric quadrupole moment of K^{40} by coupling the Q of K^{39} with that of the extra $f_{7/2}$ neutron gives $Q_{\text{theor}}=-0.036$ b, whereas the experimental value is $Q_{\text{expt}}=-0.07$ b. Similarly, Nathan and Nilson[6] find that even in K^{39}, $Q_{\text{theor}}=+0.040$ b, while $Q_{\text{expt}}=+0.09$ b. These together suggest that the polarization of the core by the valence nucleons may be a noticeable effect, and hence that $\delta\langle r^2\rangle/\langle r^2\rangle$ in K^{40} nuclei may have a nonzero value. Moreover, nonzero values of $\delta\langle r^2\rangle/\langle r^2\rangle$ have been observed in the rotational levels of deformed nuclei[7] for which comparably rough nuclear models would also predict $\delta\langle r^2\rangle=0$.

The upper limit for $\delta\langle r^2\rangle/\langle r^2\rangle$ from the earlier experiment[1] is too large to be useful. That limit, in fact, is larger than the observed value for any known nucleus. This means that the validity of the model leading to $\delta\langle r^2\rangle/\langle r^2\rangle=0$ should be tested by more precise measurement—and this, in fact, was our major purpose.

Also it was hoped that measurements of the magnetic moment μ and the electric quadrupole moment Q for the first excited level of K^{40} would be possible by using appropriate compounds. For example, the antiferromagnetic substances $KNiF_3$ and $KCoF_3$ might have had a large transferred hyperfine magnetic field at the K nucleus and the layered structure KC_8 might have generated a measurably large electric field gradient. Finally, it was expected that measurements of the temperature dependence of the second-order Doppler shift and of the resonant fraction f would lead to information on the lattice-dynamical behavior of the potassium compounds under study.

II. TECHNIQUE

In our experiment, we chose the K^{39} (n, γ) reaction to populate the Mössbauer level in K^{40}. The reasons for choosing the (n, γ) reaction rather than the (d, p) reaction are: (1) The yield of the signal γ rays can be comparatively large for a high-intensity neutron beam (10^8 neutrons/cm^2/sec in our case); and, more important (2) since most of the neutrons (~99% in our experiment) do not interact with our necessarily thin target and most of the reaction energy escapes from the target as high-energy γ rays, the heat deposited in the target is small. Thus the target can easily be cooled. This is a big advantage over the techniques in which the Mössbauer level is populated by charged-particle reactions.

A schematic diagram of the experiment is shown in Fig. 1. A thermal-neutron beam from the reactor core emerges through collimators in the reactor shielding wall. The K^{39} target produces the signal γ ray (29.4 keV) after the neutron-capture reaction. Those γ rays are detected after passing through an absorber enriched in K^{40}. Either the target or the absorber is moved in order to perform a conventional Mössbauer transmission experiment. The first beam used was at a through hole provided with a graphite scatterer. This provided a moderate flux along with a low background. To get more time than was available at this very popular facility, we moved the experiment to a temporarily unused beam hole, which had been designed wide and thin for a neutron-mirror experiment. For this hole we built a special tapered collimator consisting of alternate layers of lead and plastic; and in its exit aperture we placed a plug of plaster containing lead and Li^6 to absorb unwanted neutrons and to minimize high-energy γ rays.

In our effort to reduce the background count of our detector in the neighborhood of the 29.4-keV line of K^{40}, we found that a considerable fraction of this background is due to scattered low-energy γ rays; these were emerging from the reactor along with the neutrons. Figure 2 shows the striking reduction of the background line when a $\frac{1}{16}$-in.-thick lead sheet was mounted before the collimator exit (as shown in Fig. 1).

A. Cryostats

Since the Debye temperature of potassium in most of its compounds is well below room temperature, it is

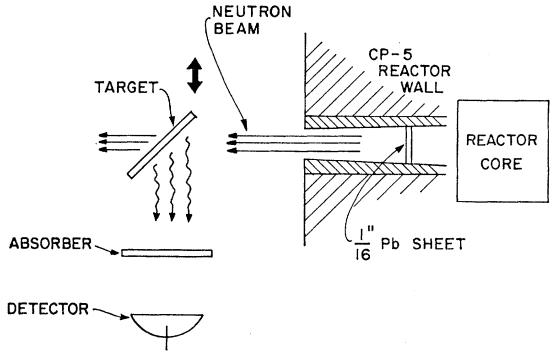

FIG. 1. Schematic diagram of the experimental setup. The double arrow shows the direction of motion of the target or absorber in the Mössbauer experiment.

[4] S. Goldstein and I. Talmi, Phys. Rev. **105**, 995 (1957).
[5] I. Talmi and S. Unna, Ann. Rev. Nucl. Sci. **10**, 353 (1960).
[6] O. Nathan and S. G. Nilson, in *α, β, and γ-Ray Spectroscopy*, edited by K. Siegbahn (North-Holland Publishing Co., Amsterdam, 1965), Chap. X, p. 618.
[7] S. Bernow, S. Devons, I. Duerdoth, D. Hutlin, J. W. Kast, E. R. Macagno, J. Rainwater, K. Runge, and C. S. Wu, Phys. Rev. Letters **18**, 787 (1967); D. Yeboah-Amankwah, L. Grodzins, and R. B. Frankel, *ibid.* **18**, 791 (1967); P. Steiner, E. Gerdau, P. Kienle, and H. T. Körner, Phys. Letters **24B**, 515 (1967).

advantageous to cool both target and absorber. (Here and in the following, "Debye temperature" is used to mean that characteristic temperature which gives the observed resonant fraction f when a monatomic Debye model is assumed for the solid.) When both target and absorber were to be kept at liquid-nitrogen temperature, the simple arrangement shown in Fig. 3 was used.

The cryostat shown here consists of a cylindrical styrofoam container E and a cover F. The space inside the container is divided into an upper and a lower part. The upper part is an aluminum can J with an annular hole; it serves as a liquid-nitrogen reservoir. The lower part, refrigerated by the cold walls of J, contains the source and the absorber.

The neutron target (source) is moved by an insulated rod C which connects through the annular hole of the can J to the moving axis of an electromechanical driver B. The thermal-neutron beam enters and leaves the cryostat directly through the styrofoam wall. The effect of the styrofoam on the neutron beam is merely to increase the background at the detector to about 10% more than that without styrofoam. This disadvantage is a small price for avoiding the difficulty of designing and handling a metal cryostat.

For some experiments the target (source) was kept at liquid-He temperature. This is necessary, especially for potassium metal, because of the very low Debye temperature of this material. For reasons of convenience, source and absorber were kept in different cryostats for these experiments, the absorber still being at liquid-nitrogen temperature. The target was mounted in the tail section of a regular liquid-helium cryostat which had been modified to allow passage of the neutron beam with minimal production of background γ radiation. The entrance and exit windows for the neutron beam had to be made fairly large and, consequently, the heat shielding of the target was not too effective. We estimate that the target temperature was $(10\pm6)°K$. Since our measurements are quite insensitive to temperature fluctuations in this range, no efforts were made to lower the temperature further or to improve the accuracy of its determination. The absorber in these experiments was kept at liquid-nitrogen temperature in a styrofoam cryostat similar to the one depicted in Fig. 3. Figure 4 shows both cryostats and the detector in their proper relative positions. Since the neutron beam is only slightly attenuated in passing through one of our cryostats, we were able to use our limited reactor time efficiently by usually running both spectrometers simultaneously, the one behind the other in the beam.

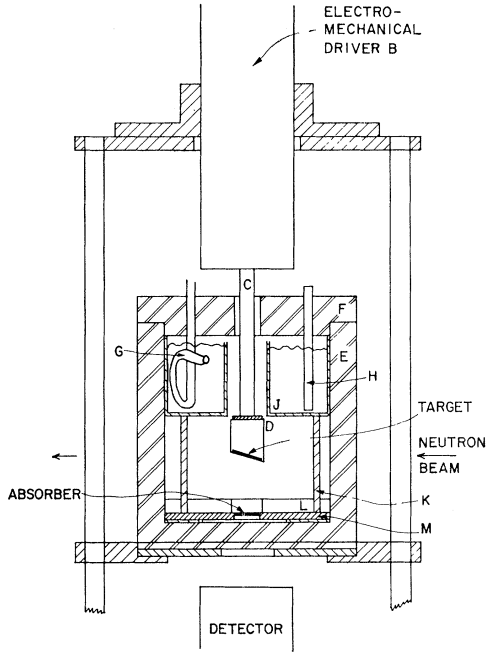

FIG. 3. Liquid-nitrogen cryostat for a Mössbauer-effect experiment with a beam of reactor neutrons. In the figure, B is the electromechanical driver, C an insulating rod connecting the driver to the target, D the target holder, G the liquid-nitrogen filling tube, H the sensing element of the automatic filling system, J the liquid-nitrogen reservoir, K the legs for J, L the neutron shielding (borated polyethylene), and M the γ shielding (lead plate).

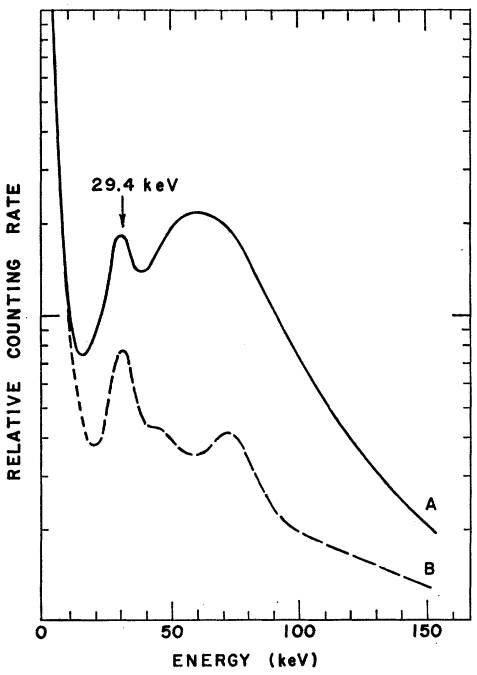

FIG. 2. γ-ray spectra detected by a 1/32-in. NaI detector. Curve A: the spectrum when the reaction is induced by an unfiltered beam of neutrons. Curve B: the spectrum when the reaction is induced by a reactor neutron beam filtered through a 1/16-in. lead sheet.

B. Mössbauer Spectrometer

When the styrofoam cryostat described in Sec. I A was used in measuring Mössbauer spectra at liquid-nitrogen temperatures, we used a standard Kankeleit-

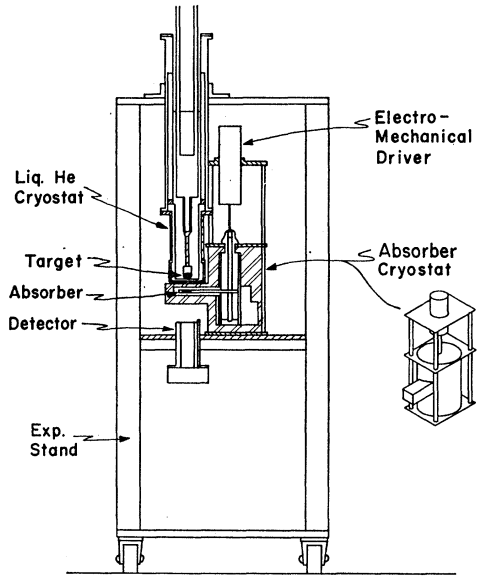

FIG. 4. Over-all experimental setup to measure the relative Mössbauer line shift between K and KF.

type[8] spectrometer (i.e., the target moved with a constant acceleration and the multichannel analyzer was in the time mode).

In measurements with the liquid-helium cryostat (Fig. 4), the moving absorber is supported by a long horizontal arm and a vertical aluminum rod. They are driven by the electromechanical driver, which is coupled to the aluminum rod by a flexible junction. Since this complexity makes the assembly somewhat flexible, it is unwise to drive this system in the constant-acceleration mode. Instead, we decided to drive the moving system sinusiodally at its resonant frequency. The reference signal for this sine wave is generated by a Hewlett-Packard model-202A function generator. In this case, the time mode of the multichannel analyzer is still used, but with a reset pulse for the address scaler derived from the function generator.

C. Targets

Since the yield of the interesting γ rays and the background are both functions of the thickness of the target, special consideration was given to the thickness of the target in order to obtain experimental results efficiently. The target thickness was usually in the range of 100–300 mg/cm^2. For some target materials, however, even optimized targets did not allow a useful experiment. For example, the compounds KI, KBr, K_2WO_3, and K_3Sb all were unusable. These difficult materials have one or more of the following properties: They contain elements with high atomic number and, consequently, have high self-absorption for the 29.4-keV γ rays from K^{40}; they contain elements which emit γ rays or characteristic x rays of energy close to 30 keV; and/or they contain nuclei with high neutron absorption cross section, in which case the K^{39} nuclei would be shielded from neutrons while at the same time a very high γ background would be produced.

After selecting a target compound and determining its optimum thickness, a disk $1\frac{1}{4}$ in. in diameter was obtained by pressing a fine powder of the compound into a mold. In some cases Lucite was used as a binder; in other cases the powder was pressed while enclosed in an aluminum foil. The latter method can give a moderately rigid disk even for noncompacting powders.

D. Absorbers

Since the natural abundance of K^{40} is only 0.0118%, it was necessary to use a sample enriched in this isotope. A KCl sample enriched to 1.9% K^{40} was obtained from Oak Ridge National Laboratory and the absorber was made by pressing the powder, with Lucite as a binder, just as in preparing the targets. The K^{40} thickness of the KCl absorber was 0.66 mg/cm^2. This gives an effective thickness $t=n\sigma f\approx 2$ at 80°K when the effective Debye temperature is taken as 180°K.

III. RESULTS AND DISCUSSIONS

A. Observations in Various Potassium Compounds

Several potassium compounds were used as targets. In particular, we selected compounds in which a magnetic field, an electric field gradient, or a variation of the s-electron density at the site of the nucleus might reasonably be expected.

All the spectra of the various potassium compounds used, either as targets or as absorbers, showed a single absorption peak whose width is no more than 1.3 times that of the one calculated from the half-life and the effective thickness. These experimental results are summarized in Table I, which lists the target material, the absorber material, the shift v_0 of the center of the Mössbauer line from $v=0$, the width β of the line, the observed amplitude α of the line, the true amplitude α_0 (corrected for background), and an effective Debye temperature Θ_D of the target material. The recoilless fraction f was calculated for these sources from the corrected dip α_0 along with the known properties of the absorber.

The fact that all the runs in Table I gave a single unshifted line indicates that (a) $\delta\langle r^2\rangle/\langle r^2\rangle$ is small and (b) the electron configuration of the potassium atom in various compounds retains its K^+ ion structure and hence does not produce large electric field gradients nor magnetic fields at the nucleus.

It should be mentioned that little, if any, evidence for radiation-damage effects is seen in these data. Since energies up to 800 eV can be given to the nucleus from

[8] E. Kankeleit, in *Mössbauer Effect Methology* (Plenum Press, Inc., New York, 1965), Vol. II, p. 47.

TABLE I. Results of experiments at liquid-nitrogen temperature. Here v_0 is the shift of the Mössbauer line from $v=0$, β is its full width at half-maximum, α is the observed amplitude of the Mössbauer line, α_0 is the true amplitude (corrected for background), and Θ_D is the Debye temperature of the target [with $\Theta_D(\mathrm{KCl})=190°$ taken as standard].

Target	Absorber	v_0 (mm/sec)	β (mm/sec)	α (%)	α_0 (%)	Θ_D (°K)
KF	KI	0.015±0.012	2.55±0.04	0.88±0.01	2.4	...
KF	KCl	−0.005±0.008	2.74±0.04	3.21±0.04	6.4	230
KCl	KCl	−0.015±0.033	3.1±0.2	0.69±0.02	2.7	190
KC_8	KCl	0.006±0.006	2.7±0.03	1.303±0.006	3.4	195
$KNiF_3$	KCl	−0.00±0.02	2.7±0.1	1.05±0.02	5.1	215
$KCoF_3$	KCl	0.01±0.03	2.9±0.1	0.60±0.01	3.9	205
KO_2	KCl	0.02±0.01	2.82±0.06	0.044±0.006	1.4	170
$KAlSi_3O_8$	KCl	−0.13±0.09	3.2±0.4	1.24±0.07	3.6	200
KN_3	KCl	0.016±0.09	2.6±0.3	0.85±0.06	2.7	190
KOH	KCl	0.01±0.04	3.0±0.2	1.88±0.05	3.0	190
KCN	KCl	−0.4±0.3	2.9±0.9	0.51±0.09	1.0	160
KH	KCl	0.05±0.04	3.2±0.3	1.42±0.05	2.7	190
KF·HF	KCl	−0.03±0.02	3.3±0.1	1.02±0.02	2.1	180

the γ-ray emission following neutron capture, it is conceivable that disruption of the lattice could affect the Mössbauer emission; a small number in the last two columns of Table I might be explained by such a mechanism. In cases in which the Debye temperatures are known approximately from other evidence (as described in Sec. III B), such radiation-damage effects are too small to be observed.

B. Measurement with a KF Target and a KCl Absorber

The target material that gives rise to the largest Mössbauer effect is potassium fluoride. With a KF target it was therefore possible to take a reasonably accurate Mössbauer spectrum in a comparatively short time (~6 h). Since the experimental equipment and techniques evolved steadily in the course of the experiment, we reran the KF-KCl measurements several times—both to take advantage of improvements and to assess their value. Thus the KF-KCl experiment became the standard test to evaluate the latest changes in the neutron collimators, shielding, detectors, etc.; the observed amplitude α of the Mössbauer line was squared and multiplied by the counting rate R to obtain the figure of merit $R\alpha^2$. Moreover, the stability of the over-all experimental system could be tested by examining the results of several runs of the same experiment. If the results fluctuate only in the anticipated statistical fashion, then the over-all experimental apparatus is functioning in a stable, reproducible manner.

In order to estimate the reproducibility of the experiment we plotted the values of v_0 for the repeated runs in chronological order, as shown in Fig. 5. Since the scatter among the several runs is not much greater than the uncertainty in each experiment, there seems to be no appreciable drift. More quantitatively, this can be shown by comparing the weighted standard deviation of the experimental points (0.007 mm/sec) with the errors of single runs (0.005–0.010 mm/sec). Comparison with similar data in the literature,[1,2] also plotted in this figure, shows the great improvements in experimental techniques that have been obtained.

C. Measurements with a KF Target and KI Absorber

According to Shirley,[9] the isomer shift can be described by the equation

$$\delta=\tfrac{2}{5}\pi Ze^2S'(Z)\langle r^2(A)\rangle[\,|\,\psi_a(0)\,|^2-|\,\psi_s(0)\,|^2]\delta\langle r^2\rangle/\langle r^2\rangle. \quad (1)$$

Here Z is the atomic number and A the atomic weight of the Mössbauer nucleus, r is its radius, $\psi_a(0)$ and $\psi_s(0)$ are the electron wave functions at the nucleus for absorber and source atom, respectively, $S'(Z)$ is a relativistic correction tabulated in Ref. 6, and the fraction $\delta\langle r^2\rangle/\langle r^2\rangle$ is the mean square fractional change in the nuclear radius as a result of the transition from the first excited state to the ground state.

The largest isomer shift δ between potassium halides would probably be that for a KF target and KI absorber, in analogy with the results of the Mössbauer experiments[10] on the Cs^{133} halides. In the latter, the isomer shift between a CsF source and a CsI absorber was found to be 0.031±0.004 mm/sec. If

$$[\,|\,\psi_a(0)\,|^2-|\,\psi_s(0)\,|^2]\delta\langle r^2\rangle/\langle r^2\rangle$$

in Eq. (1) were assumed to be the same in potassium as in cesium, the isomer shift δ between KI and KF would be expected to be 0.0025 mm/sec. The decreased shift in the potassium experiment results from the combination of several factors, including the relativistic enhancement of $|\,\psi(0)\,|^2$, the change in nuclear radius (as discussed in Ref. 9), and the atomic number. On

[9] D. A. Shirley, Rev. Mod. Phys. **36**, 339 (1964).
[10] A. J. F. Boyle and G. J. Perlow, Phys. Rev. **149**, 165 (1966).

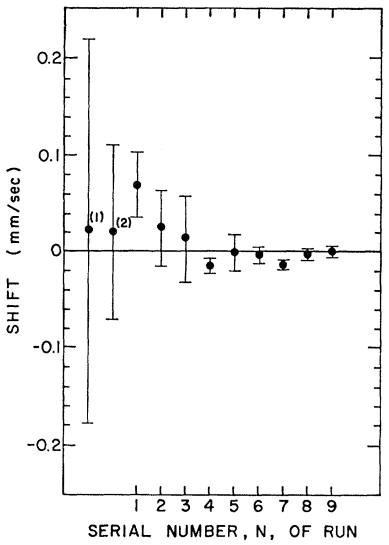

FIG. 5. Experimental values of the Mössbauer line shifts found in separate runs. The point marked (1) was taken from Ref. 1 and (2) from Ref. 2. (There is some uncertainty concerning the chemical form of the target in Ref. 2.) Other data are from the present work and are plotted in chronological order.

the other hand, the thermal shift due to the 40°K difference between the Debye temperatures of the two solids at 80°K is $v_{th}=0.01$ mm/sec. [Here we have taken $\Theta_D(\mathrm{KF})=240°\mathrm{K}$ and $\Theta_D(\mathrm{KI})=200°\mathrm{K}$.] The experimental result for this pair of halides (Table I) is

$$v_0=0.015\pm0.012 \text{ mm/sec.} \quad (2)$$

This result indicates that the major contribution to this shift in the Mössbauer line is due to the thermal effect. Of course $\delta|\psi(0)|^2$ for these two ionic crystals is expected to be small.

D. Potassium Graphite (KC_8)

Among the various chemical compounds used as targets, potassium graphite KC_8 has the most interesting crystal structure. This is an intercalation compound[11] in which the carbon atoms form stable sheets of linked hexagons. The structure of each sheet is identical with that of graphite; but the atoms in successive carbon planes in KC_8 are in identical positions, whereas the atoms in the successive carbon planes in graphite are displaced from each other in a sequence *ABCABC* or *ABABAB*. The interplanar distance of KC_8 is 5.41 Å, whereas that of graphite is only 3.35 Å. The potassium atoms always occupy positions above or below the middle of a hexagonal ring of atoms. Each K atom gives up its outermost *s* electron to a conduction band. The result is that the thermal and electrical conductivity are much higher in KC_8 than in graphite.

From the point of view of the Mössbauer effect, one consequence of this is that $|\psi(0)|^2$, the electron density at the K nucleus in KC_8, may differ from that of the potassium ion. There has been a report[12] that a Knight shift has been observed in CsC_8. It is reasonable to assume that the conduction electrons in KC_8 have some *s* character, in agreement with the above result. A second consequence is that an electric field gradient (EFG) at the K nucleus may result from the layered structure of the graphite. This argument is supported by the observation of a splitting in the Mössbauer spectrum in cesium graphite CsC_8.[13] Unfortunately, the data on the Mössbauer effect in CsC_8 are still tentative and we are not able to make very certain judgments from these data.

Nevertheless, we made a careful Mössbauer measurement on KC_8 (as target), but the result was disappointing. The Mössbauer spectrum of KC_8 is a single line with $\beta=2.70\pm0.03$ mm/sec and $\Delta v_0=0.006\pm0.006$ mm/sec. This result shows that the quadrupole splitting is very small. The upper limit of the line broadening due to possible quadrupole splitting is less than 0.13 mm/sec. If we assume $Q_e/Q_g\approx1$, then it follows that $e^2qQ<12$ MHz.

E. Measurement of Mössbauer Line Shift between K and KF

This experiment is the main part of the work. Its purpose was to use the isomer shift of K^{40} between potassium metal and KF to evaluate the fractional difference $\delta\langle r^2\rangle/\langle r^2\rangle$ between the ground state and the first excited state.

The same KCl absorber, kept at liquid-nitrogen temperature in a separate cryostat, was used throughout these experiments. Two target materials and three temperatures were used in the four experiments. In experiment I, potassium metal was used as a target and liquid helium was used as a coolant. The same KF target was used for the other three experiments but its temperature was changed. It was maintained at 10°K by liquid helium in experiment II, at 55°K by solid nitrogen in III, and at 78°K by liquid nitrogen in IV. Experiments I and II afford a direct comparison of the line shift between K and KF.

Experiments II, III, and IV serve to check the temperature behavior of the thermal shift, from which in turn one can determine the Debye temperature for K in KF. On the other hand, we did not plan measurements on potassium metal at temperatures other than that of the liquid helium because of its extremely low Debye temperature (about 90°K). Each of the four measurements was divided into numerous equal time intervals, and the set of data obtained from each subrun

[11] W. Rüdorff, in *Advances in Inorganic Chemistry and Radiochemistry* (Academic Press Inc., New York, 1959), Vol. 1, p. 223.

[12] V. Jensen, D. E. O'Reilly, and Tung Tsang, J. Chem. Phys. (to be published).

[13] G. J. Perlow (private communication).

TABLE II. Results on the K-KF relative line-shift measurements.

Experiment No.	Target	T (°K)	α (%)	β (mm/sec)	v_0 (mm/sec)
I	K	10±6	1.26+0.05	3.32±0.13	−0.065±0.006
II	KF	10±6	7.37±0.20	3.42±0.11	−0.012±0.005
III	KF	55	4.74±0.47	3.39±0.12	0.006±0.005
IV	KF	78	4.41±0.10	3.24±0.09	0.015±0.004

was analyzed individually. The scattering of the data obtained from those subruns was no greater than the statistical error of a single subrun. These results show that the experiments were normal and reproducible.

Table II lists the results of the computer analysis of the sum of all the subruns. The values of α, β, and the relative shift v_0 to an arbitrarily selected channel are listed in the third, fourth, and fifth columns, respectively. In each case, the quoted uncertainties reflect only the statistical errors. The Mössbauer line shift between a KF source at 10°K and a K metal absorber at the same temperature is

$$v_0=0.053\pm0.008 \text{ mm/sec},$$

where a positive value of v_0 means that the source and absorber are approaching each other. This line shift corresponds to the sum of the isomer shift δ and the thermal shift v_{th}, i.e.,

$$v_0=\delta+v_{\text{th}}. \tag{3}$$

The determination of the isomer shift and, consequently, of the relative change $\delta\langle r^2\rangle/\langle r^2\rangle$ in the nuclear radius will be discussed below. Obviously, to obtain δ from our measurements of v_0, a value for the thermal shift v_{th} is needed.

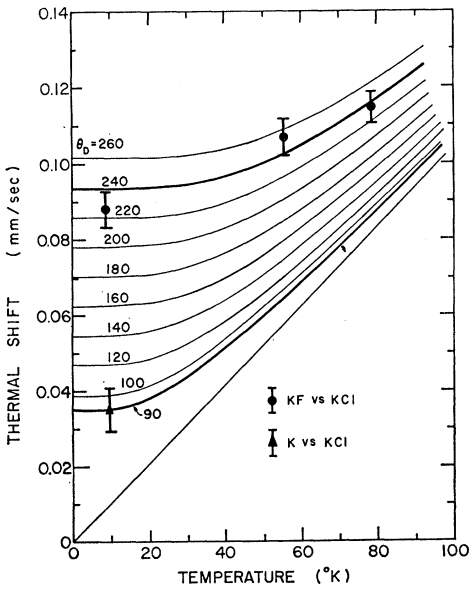

FIG. 6. Thermal shifts of KF at 10°, 55°, and 78°K and of K at 10°K. The curves were calculated relative to a fictitious absorber whose Debye temperature is 0°K and whose temperature is 0°K. Here the Debye temperature of K is assumed to be 90°K. The points for K metal and KF sources and a KCl absorber are from experiments I–IV.

The relation between the data points obtained in experiments I–IV and the Debye temperatures of K in potassium metal and in KF may be seen in Fig. 6. This figure shows how the thermal shift v_{th} in K^{40} varies with temperature for various values of the Debye temperature Θ_{Ds} of the source. The relation between the thermal shift and the temperatures of both source and absorber may be expressed[14] as

$$v_{\text{th}}=(1/2mc)[(9/8)k\Theta_{Ds}+3kT_sD(X_s) - (9/8)k\Theta_{Da}-3kT_aD(X_a)], \tag{4}$$

where

$$D(X)=\frac{3}{X^3}\int_0^X\frac{\xi^3d\xi}{e^\xi-1},$$

and Θ_{Ds} is the Debye temperature of the source crystal, Θ_{Da} the Debye temperature of the absorber crystal, $X_s=\Theta_{Ds}/T$, and $X_a=\Theta_{Da}$.

The curves in Fig. 6 were computed from Eq. (4) by setting both Θ_{Da} and T_a equal to zero. Inspection of Eq. (4) shows that this merely suppresses an additive constant.

The data points obtained from experiments I–IV were superimposed on this graph by choosing $\Theta_{Ds}=90$°K for potassium metal on the basis of the specific-heat measurement.[15] After this choice, the position of the KF data points are automatically determined. They seem to group very nicely around the curve with the parameter $\Theta_{Ds}=240$°K. The mean deviation of these points is less than the experimental error.

F. Measurement of the Recoilless Fraction as a Function of the Source Temperature

It is impossible to determine the isomer shift between K and KF unless the thermal shift between K and KF is known. Therefore an experiment was planned to confirm our earlier measurements of the Debye temperature of KF.

[14] R. V. Pound, in *Proceedings of the International Conference on the Mössbauer Effect, Saclay, France, 1961*, edited by D. M. J. Compton and A. H. Schoen (John Wiley & Sons, Inc., New York, 1962), p. 222.

[15] L. M. Roberts, Proc. Phys. Soc. (London) **B70**, 744 (1957).

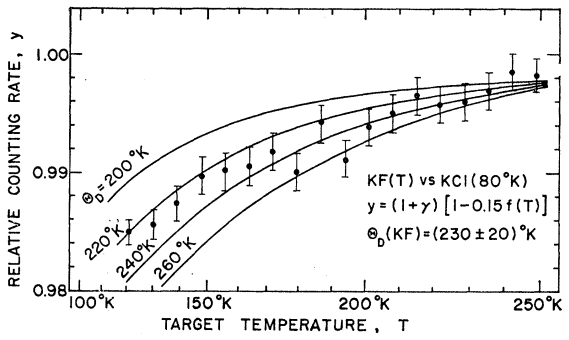

FIG. 7. The experimental results (points) on the recoilless fraction $f(T)$ as a function of the target temperature. The target is KF. The curves give the calculated relative transmission $y(T)$, through the Mössbauer absorber with known effective thickness. In addition, the background ratio is given by a separate measurement. These calculated curves have then been shifted along the y axis a small amount γ to fit the experimental data.

The experiment is the measurement of the counting rate $R_{v=0}$ of the transmitted γ ray as a function of the temperature of the target. The rate $R_{v=0}$ depends on the temperature in accordance with the relation[5]

$$R_{v=0}(T)=R_{\mathrm{BG}}+R_s e^{-\mu t}\{1-f_\Theta(T)[1-e^{-\frac{1}{2}t_e}J_0(\tfrac{1}{2}it_e)]\}, \tag{5}$$

where R_{BG} is the counting due to the background and does not depend on the presence of the absorber, R_s is the counting rate of the resonant γ ray when the absorber is not present, t is the thickness of the absorber, μ is the γ-ray attenuation coefficient of the absorber material at 29.4 keV, $f_\Theta(T)$ is the recoilless fraction of the emitted 29.4-keV γ ray from the target at temperature T and Debye temperature Θ_D, and t_e is the effective thickness of the absorber for the Mössbauer γ ray. After dividing $R_{v=0}$ by its temperature-independent part, we find that the reduced function $y(T)$ is

$$y(T)=R_{v=0}(T)/(R_{\mathrm{BG}}+R_s e^{-\mu t})=1-c_0 f_\Theta(T), \tag{6}$$

where

$$c_0=n_s e^{-\mu t}/(R_{\mathrm{BG}}+R_s e^{-\mu t})[1-e^{-\frac{1}{2}t_e}J_0(\tfrac{1}{2}it_e)]. \tag{7}$$

In Eq. (6), c_0 can be calculated from the information on the signal-to-background ratio and on the equivalent resonant thickness t_e of the absorber. Then $y(T)$ can be calculated numerically for a particular Debye temperature. To measure $y(T)$ experimentally, the source and absorber were kept at rest with respect to each other and each temperature interval (from T to $T+\Delta T$) was associated with a particular channel I of the multichannel analyzer. Counts were simultaneously accumulated in two halves of the analyzer—one half accumulating the count $n_r(I)$ from the resonant γ ray, the other accumulating the count $n_0(I)$ from a nonresonant part of the γ-ray spectrum. Then $y_{\mathrm{expt}}(T)$ is obtained from

$$y_{\mathrm{expt}}(T)=C[n_r(I)/n_0(I)],$$

where C is a parameter to be adjusted to fit the properties of Eq. (6), i.e.,

$$\lim_{T\to\infty} y_{\mathrm{expt}}(T)=1, \tag{8}$$

$$y(T_0)=y_{\mathrm{expt}}(T_0)=1-c_0 f(T_0)=1-\alpha. \tag{9}$$

Equation (8) means that the resonant absorption will vanish when the temperature of the source is considerably higher than the Debye temperature; and Eq. (9) means that y is equal to one minus the amplitude α of the resonance peak when a Mössbauer spectrum is taken at temperature T_0.

In practice, C is replaced by $C'/(1+\gamma)$, where C' is a constant obtained by a rough estimate from the relations (8) and (9), and γ is a parameter to be adjusted when the y_{expt} points are fitted to the value of $y(T)$ calculated for each Debye temperature by use of Eq. (6).

The fitting was done graphically, by making use of the strong variation of the curvature of $y(T)$ with Θ_D. The resultant best fit for the KF target is

$$\Theta_D=(230\pm 20)^\circ\mathrm{K}.$$

Figure 7 shows the experimental points and the fitting curves for the case of KF versus KCl. Each experimental point is the average of ten analyzer channels.

The importance of this result to the final accuracy of the $\delta\langle r^2\rangle/\langle r^2\rangle$ measurement was not reflected in the duration of this experimental run. The quoted uncertainty of $\pm 20^\circ$K could have been reduced by a factor of four by running for several days instead of several hours. At the time these data were taken, it was assumed that an accurate value of Θ_D could be obtained from specific-heat data on KF.

G. Estimation of the Debye Temperatures of K and KF

As was mentioned in the discussion of Eq. (3), a value for the thermal shifts of both K and KF would permit us to obtain the isomer shift between these two materials from our measured value of the relative Mössbauer line shift between K and KF.

Equation (4) gives the relation between the thermal shift and the Debye temperatures of both the source and the absorber. In the following we discuss our choices for Θ_D for potassium metal and KF, which we used for the determination of the thermal shifts between these two substances. All relevant data are assembled in Table III.

Our single determination of the Debye temperature

of potassium metal was made by computing it from the single observed amplitude of the Mössbauer resonance line. This value is

$$\Theta_D(K) = (90\pm8)°\text{K}.$$

For confirmation of this value we may look to Θ_D values extracted from specific-heat measurements.[15] In the range from $0<T<20°$K, these values drop from 90° down to 83° and return to 95°. We feel that our experimental value for the Debye temperature should be compared with the specific-heat result[15] at 0°K, namely $(89.1\pm5)°$K.

As seen in Table III, four different values for the Debye temperature of KF were obtained by different methods in the present work. The weighted mean of these four Debye temperatures is

$$\Theta_D(\text{KF}) = (236\pm20)°\text{K}.$$

The Debye temperatures obtained from the previous Mössbauer experiment[1] differ moderately from our result. It seems that their results are strongly dependent on the precise determination of the background in the pulses from the single-channel analyzer. In their experiment, this background was not measured, but only estimated from the shape of the γ-ray pulse-height spectra. In our case, the γ-ray spectra were studied as a function of attenuation in lead absorbers with thicknesses ranging from zero to 120 mg/cm^2. This provided a better criterion by which 29.4-keV pulses due to γ rays emitted by the target could be distinguished from those created in the detector itself. In our further analysis, the effective Debye temperatures from Ref. 1 will not be used. In addition, we were surprised to find no precise specific-heat data for KF. Therefore the above-mentioned weighted mean of the four effective Debye temperatures from the present work is used.

TABLE III. Estimate of the Debye temperatures of K and KF from various methods.

Target material	Method of measurement	T (°K)	Θ_D (°K)	Ref.
K	α (amplitude of the Mössbauer line)	10±6	90±8	a
K	α	4	60±(?)	b
K	Specific heat	0	89.1±0.5	c
KF	α	78	235±20	d
KF	$\alpha(10/\alpha(78)$	10, 78	247±25	e
KF	$f(T)$ (recoilless fraction)	100–200	230±20	a
KF	v_{th} (thermal shift)	10, 55, 78	205±55	a
KF	α	4	145±(?)	b
KF	α	78	190±(?)	b

[a] Present work.
[b] D. W. Hafemeister and E. B. Shera, Phys. Rev. Letters **14**, 593 (1965).
[c] L. M. Roberts, Proc. Phys. Soc. (London) **B70**, 744 (1957).
[d] Present work. See Table I.
[e] Present work. The data used for the calculation of the Debye temperature were taken from Table II.

H. Estimate of the Isomer Shift between K and KF and of $\delta\langle r^2\rangle/\langle r^2\rangle$ for K^{40}

For the reasons explained in Sec. III G, the Debye temperatures have been taken to be

$$\Theta(\text{K}) = (90\pm8)°\text{K} \quad \text{for} \quad \text{K},$$

$$\Theta(\text{KF}) = (236\pm20)°\text{K} \quad \text{for} \quad \text{KF}.$$

When these data are substituted in Eq. (4), the thermal shift v_{th} between KF and K is found to be

$$V_{\text{th}} = 0.055\pm0.009 \text{ mm/sec}.$$

Then by Eq. (3), the isomer shift δ is

$$\delta = v_0 - v_{\text{th}} = -0.002\pm0.012 \text{ mm/sec}. \qquad (10)$$

Equation (1) is a relation between δ and $\delta\langle r^2\rangle/\langle r^2\rangle$. This relation becomes simple after substituting the numerical data. Then according to Shirley,[9] the shift in mm/sec is

$$\delta = (1/0.0214)\Delta\,|\psi(0)|^2\delta\langle r^2\rangle/\langle r^2\rangle, \qquad (11)$$

where $\Delta|\psi(0)|^2$ is the difference between the s-electron density in K and that in KF in atomic units (i.e., in units of a_0^{-3}, where $a_0 = 0.52918\times10^{-8}$ cm). Since our upper limit on the shift is $\delta \leq 1.2\times10^{-2}$ mm/sec, it follows that

$$\delta\langle r^2\rangle/\langle r^2\rangle \leq (2.66\times10^{-4})/\Delta\,|\psi(0)|^2, \qquad (12)$$

where $\Delta|\psi(0)|^2$ can be calculated theoretically. As a first approximation to the charge-density difference between the potassium ion and the metal, the charge density due to a 4s electron in a free potassium atom will be used. This neglects the (probably small) effect of the rearrangement of the inner electrons in the K^+ ion. Shirley[9] gives $|\psi_{4s}(0)|^2 = 1.11$ per atomic volume for 4s electrons. This value agrees with the value $[(|\psi_{4s}(0)|^2 = 1.06$ per atomic volume$]$ calculated on the basis of the results of Skillman and Herman.[16]

By using Hartree-Fock calculations with an improved method for electron correlations, Wilson[17] obtained the difference between the value of $|\psi(0)|^2$ for a free potassium atom and a free K^+ ion. This result is 0.76 per atomic volume. Since Wilson's method seems to be a better approximation to physical reality, his value will be used for further calculation.

[16] S. Skillman and F. Herman, *Atomic Structure Calculation* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).
[17] M. Wilson (private communication).

For a second approximation, the difference between the free atom and the metal must be considered. The density $|\psi(0)|^2$ of $4s$ electrons in pure K metal is complicated to calculate. Most of the band-theory calculations are done with no particular interest in the behavior near the nucleus, and the pseudopotential calculations are completely useless for the present purpose. Shirley[9] has presented reasons for believing that a better approximation might be obtained by taking $|\psi(0)|^2=0.7|\psi_a(0)|^2$, the electron densities at the nucleus being $|\psi(0)|^2$ for the s electrons of the conduction band and $|\psi_a(0)|^2$ for the $4s$ electrons in a free atom.

In the light of this discussion, the most reliable value for $\Delta|\psi(0)|^2$ would be 0.7 times the value calculated by Wilson.[18] Then the upper limit of $\delta\langle r^2\rangle/\langle r^2\rangle$ is

$$\delta\langle r^2\rangle/\langle r^2\rangle<5.0\times10^{-4}.$$

IV. CONCLUSION

The conclusion at the end of Sec. III H was that $\delta\langle r^2\rangle/\langle r^2\rangle$ for the K^{40} nucleus must be quite small and that, with some confidence, its upper limit can be given as

$$\delta\langle r^2\rangle/\langle r^2\rangle<5.0\times10^{-4}.$$

This result indicates that the simple vector-coupling calculation of $\delta\langle r^2\rangle/\langle r^2\rangle$ for the K^{40} nucleus, which gives exactly zero, is still true within the uncertainty 5×10^{-4}.

In using this result, one should keep in mind the various measurements, parameters, and assumptions on which we have based our estimate of $\delta\langle r^2\rangle/\langle r^2\rangle$. These are: (a) The over-all Mössbauer line shift between K and KF at liquid-helium temperature was measured to be 0.053 ± 0.008 mm/sec. (b) Potassium metal is assumed to be a Debye solid with an effective Debye temperature equal to 90 ± 8°K at liquid-helium temperature. (c) Similarly, KF has an effective Debye temperature equal to 236 ± 20°K at liquid-helium temperature. (d) The value for the difference $\Delta|\psi(0)|^2$ between the electron densities at the nuclei of K and KF was based on (1) Wilson's calculation[18] of the difference $\Delta|\psi(0)|^2$ between a free potassium atom and a free K^+ ion and (2) a correction factor defined as the ratio ξ' of the wave function for the $4s$ electrons in the conduction band of potassium metal to the wave function for the $4s$ electrons in a free potassium atom, both wave functions being evaluated at the nucleus. (We used $\xi'=0.7$ as suggested by Shirley.[9])

[18] Y. Disatnik, D. Fainstein, and H. J. Lipkin, Phys. Rev. **139**, A292 (1965).

Note especially that the usefulness of increasing the accuracy of measurement a is severely limited by the present uncertainty in assumptions b and c. No precise Debye temperature of KF is available. In any case, a Debye solid is only a first-order approximation to a real crystal. Moreover, even if one could get precise data on the internal energy of K and KF, the lack of a precise and practical theory to deduce useful values from these data would still render the Debye temperature uncertain. (For example, the Debye temperature computed from the specific-heat data on KF needs to be modified[18] before it can be used as the Θ_D in the Mössbauer effect.) In addition, the induced radiation damage due to the preceding high-energy γ-ray emissions of the target nuclei may limit the direct application of the reduced internal energy to the target crystal. For these reasons, we conclude that our measurement is the best that can be justified so far, and that more accurate measurements on δ will have no physical significance unless the uncertainty in the thermal shift can be overcome by both theoretical and experimental efforts.

It should be pointed out that the measurements reported here for $f(T)$ are by no means at their limits of accuracy. Therefore, although it does seem clear that little useful chemical or magnetic information can be found by use of the Mössbauer effect in K^{40}, lattice dynamical measurements utilizing potassium do seem to be practical. For example, it may be profitable to study the ferroelectrics KH_2PO_4 or $K_2Fe(CN)_6\cdot3H_2O$ with this technique.

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