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Isomer Shifts and Mössbauer-Effect Efficiencies in Intermetallic Compounds of Europium

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Recoilless absorption measurements of the 97- and 103-keV γ rays of Eu^{153} in variuos intermetallic compounds of Eu were carried out. The results obtained for the isomer shifts were compared with those obtained previously for the 21.7-keV transition of Eu^{151} and found to be consistent with the existing theories, according to which, ΔE can be expressed as a product of a nuclear factor and an electronic factor. Anomalies found in the isomer shifts in Eu metal are very probably a result of the very low Debye temperature of the metal and the existence of impurities in the metal. The Debye temperatures of the intermetallic compounds of Eu estimated from the size of the recoilless absorption effects lie in the range between 160 and 200°K. From the analysis of the absorption spectrum of the 103-keV γ rays of Eu^{153} in Eu metal, the Debye temperature of Eu metal at 4° was estimated to be (94 ± 6)°K.

INTRODUCTION

THE main purpose of the present work was to check the validity of the existing theories of isomer shifts.[1–3] These shifts between the centroids of the recoilless absorption spectra corresponding to various absorbers are usually explained in terms of the finite nuclear volume effect which represents the change, from one absorber to another, in the modification of the nuclear transition energy caused by electrons overlapping the finite nuclear volume. Shifts produced by the difference in the thermal lattice energy between various absorbers are usually relatively small and may, in most cases, be neglected.

According to the existing theories, the isomer shift ΔE between the absorption lines of two absorbers, "a" and "b," is given by

$$\Delta E=(K_a-K_b)\Delta F. \tag{1}$$

The symbol ΔF is a nuclear factor determined by the charge distributions in the excited and ground nuclear levels involved in the γ transition and does not depend on the chemical environment. K_a and K_b are electronic coefficients proportional to the total electron densities at the nucleus in the absorbers "a" and "b". In the derivation of Eq. (1), the effect of the polarization of the nucleus by the electrons was neglected. Such effects have been suggested by Breit *et al.*[4] and have also been discussed by Reiner and Wilets[5] who estimated the quadrupole polarization of deformed nuclei.

The validity of Eq. (1) can be checked by a comparison of the isomer shifts obtained for various γ-ray transitions of isotopes of the same element. The 21.7-keV transition of Eu^{151} and the 97- and 103-keV transitions of Eu^{153} are very suitable for such a comparison because of the large shifts obtained for them. According to Eq. (1), the ratio of the isomer shifts corresponding to two Eu γ lines $\Delta E(\gamma_1,\mathrm{a},\mathrm{b})/\Delta E(\gamma_2,\mathrm{a},\mathrm{b})$ should be given by a constant, independent of the absorbers chosen, equal to $\Delta F(1)/\Delta F(2)$. Thus, if the isomer shifts of the 97- or 103-keV γ lines are plotted as a function of the shifts of the 21.7-keV line, all points should lie on a straight line passing through the origin. Preliminary recoilless absorption measurements carried out by Atzmony and Ofer with Eu_2O_3, Eu metal, and $EuSO_4$ absorbers were interpreted as showing that Eq. (1) is not always correct.[6] When additional data concerning isomer shifts in EuS and $EuCl_2$ were published by Steichele *et al.*[7] it became clear that the absorber for which relation (1) does not seem to hold is Eu metal. In order to find out whether the anomaly in Eu metal is associated with some specific properties of conduction electrons, we have measured the recoilless absorption spectra of the 97- and 103-keV γ lines of Eu^{153} in several intermetallic compounds of Eu: $EuAl_2$, $EuAl_4$, $EuCu_2$, $EuPt_2$, $EuRh_2$, and $EuPd_3$. We have also repeated the absorption measurements in a Eu metal absorber. The isomer shifts of the 21.7-keV γ rays in these intermetallic compounds were measured previously by Wickman *et al.*[8,9] The shifts in $EuRh_2$ and $EuPd_3$ show, according to Wickman *et al.*,[9] that the Eu ion is trivalent in them. In $EuAl_2$, $EuAl_4$, $EuCu_2$, and $EuPt_2$, and also in Eu metal, the Eu ion is divalent.

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* On leave from The Hebrew University, Jerusalem, Israel.

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Steichele *et al.*[10] have very recently published results of isomer shift measurements of the 21.7- and 103-keV γ rays in EuO, EuB_6, $EuSO_4$, and Eu metal. Their conclusions concerning the origin of the "anomaly" in Eu metal are similar to those drawn in the present paper.

The Debye temperatures of all the compounds investigated in the present work were estimated from the size of the effects obtained, using the Debye-Waller relation.[11]

EXPERIMENTAL DETAILS

The sources used were Sm^{153}, in the form of Sm_2O_3, and Gd^{153}, in the form of Gd_2O_3. The Sm^{153} can be regarded as emitting a pure 103-keV γ ray. With the Gd^{153} source, both the 97- and the 103-keV states are populated by electron capture. The recoilless absorption spectra obtained with the Gd^{153} source were corrected for the effects obtained from the 103-keV γ rays, and the pure 97-keV γ-ray contributions were deduced. The effects corresponding to the 103-keV γ rays were estimated from the spectra obtained for these γ rays using the Sm^{153} source, taking into account the known ratio of the intensitites of the 97- and 103-keV γ rays emitted in the decay of Gd^{153}.[12] These corrections are very small, as may also be calculated theoretically, taking into account the energies, internal conversion coefficients, and lifetimes of the transitions. (The area corresponding to the 103-keV transition is about 0.5% of the total area of the absorption lines.)

The absorbers used were $EuAl_2$, $EuAl_4$, $EuCu_2$, $EuRh_2$, $EuPd_3$, $EuPt_2$, Eu_2O_3, and Eu metal. The Mössbauer drive used was similar to the one described by Cohen *et al.*[13] The measurements were carried out with both source and absorber at 4.2 or 20°K. The experimental arrangement for cooling the source and absorber was very similar to that described in a previous work.[14] The γ-radiations were detected by a NaI scintillation counter.

EXPERIMENTAL RESULTS

The recoilless absorption spectra of the 97-keV γ ray of Eu^{153} in $EuAl_4$, Eu metal, Eu_2O_3, and $EuRh_2$ are shown in Fig. 1. Figure 2 shows the absorption spectra of the 103-keV γ rays in $EuAl_2$, $EuCu_2$, Eu_2O_3, and $EuPd_3$. The results obtained for the isomer shifts of the 21.7-keV transition[8,9] of Eu^{151} and for the 97- and 103-keV transitions of Eu^{153} are summarized in Table I. (All the shifts are measured relative to the Eu_2O_3

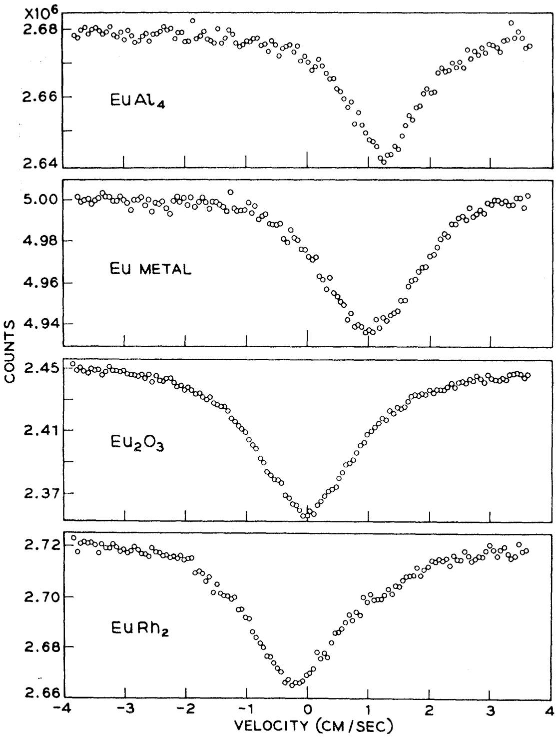

FIG. 1. The absorption of the 97-keV γ rays of Eu^{153} in $EuAl_4$, Eu metal, Eu_2O_3, and $EuRh_2$ at 20°K as a function of relative velocity between source and absorber.

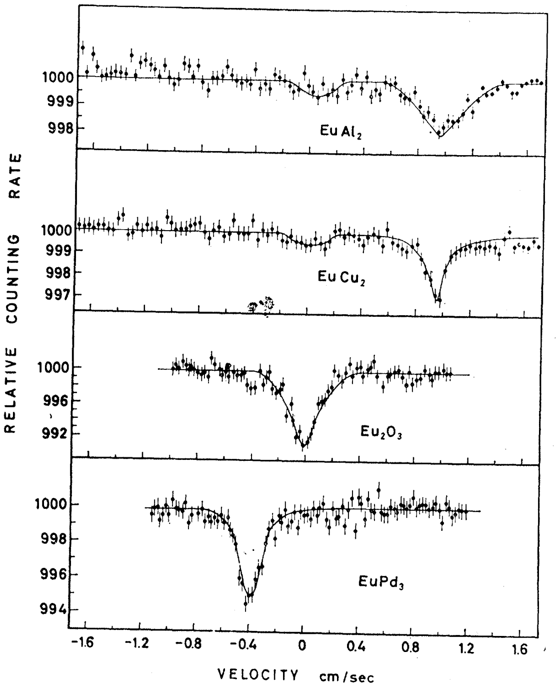

FIG. 2. The absorption of the 103-keV γ rays of Eu^{153} in $EuAl_2$, $EuCu_2$, Eu_2O_3, and $EuPd_3$ at 20°K as a function of relative velocity between source and absorber.

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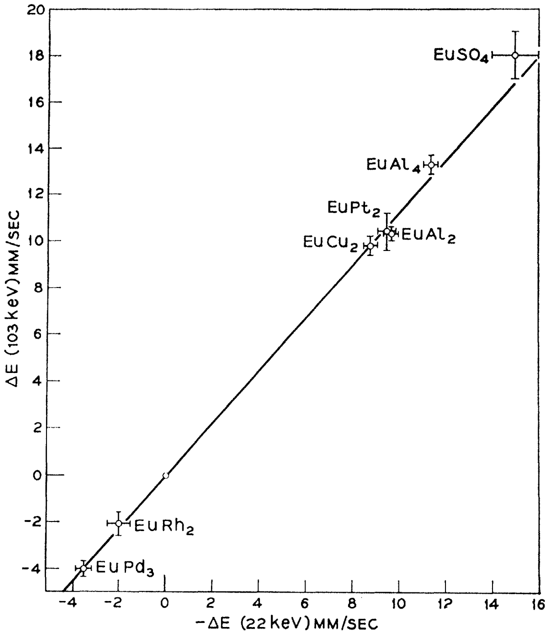

FIG. 3. Isomer shifts of the 103-keV transition in Eu^{153} versus isomer shifts of the 21.7-keV transition in Eu^{151}.

absorption lines.) Figure 3 shows a graph of the isomer shifts of the 103-keV γ line as a function of the shifts of the 21.7-keV γ line for the various absorbers. Figure 4 shows the isomer shifts of the 97-keV γ line as a function of the shifts of the 21.7-keV γ line. (The value for $EuSO_4$ is taken from Ref. 6.) In both cases, the experimental points lie on straight lines passing through the origin, indicating that within the limits of errors of the experiments the classical theory of isomer shift is correct. The value obtained for the ratio ΔE(103 keV)/ΔE(21.7 keV) is -1.14 ± 0.05, and that obtained for ΔE(97 keV)/ΔE(21.7 keV) is -1.03 ± 0.05 when the isomer shifts are measured in Doppler velocity units. The value obtained for the ratio ΔE(103 keV)/ΔE(21.7 keV) is within the limits of the errors the same as that obtained by Steichele *et al.*[10] for EuO, $EuSO_4$, and EuB_6, and that derived for EuS and $EuCl_2$ from the measurements of Brix *et al.*[15] and Steichele *et al.*[7]

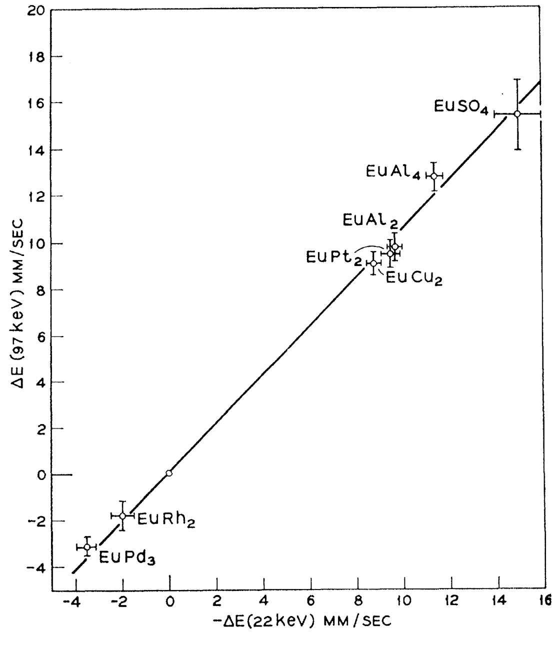

FIG. 4. Isomer shifts of the 97-keV transition in Eu^{153} versus isomer shifts of the 21.7-keV transition in Eu^{151}.

The recoilless absorption spectrum of the 103-keV γ rays in a 600-mg/cm^2 Eu metal absorber at 4.2°K is shown in Fig. 5. For comparison, the absorption spectrum in $EuAl_2$ at 4.2°K is also shown in Fig. 5. It is seen that the absorption line obtained with the Eu metal absorber is much broader than that corresponding to the $EuAl_2$ absorber, although the magnetic hyperfine fields in the metal and in $EuAl_2$ at 4.2°K are almost identical[8] (~270 kOe[8]). The arrow marked near the metal spectrum in Fig. 5 indicates the position expected for the centroid of the absorption line in the metal from the known shift of the 21.7-keV γ line of Eu^{151} in Eu metal,[14] assuming that for the metal also, $\Delta E(103\ \text{keV})/\Delta E(21.7\ \text{keV}) = -1.14$. It seems, therefore, that part of the absorption line obtained with the metallic Eu absorber corresponds to impurities in the metal. It is really known that Eu metal is very active chemically and that it is extremely difficult to produce pure Eu metal samples. The centroids of the 97- and the 103-keV absorption lines obtained with the Eu metal absorber lie midway between the positions expected for Eu metal and EuO. Thus, it is possible that the main impurity contributing to the absorption spectra is EuO. Two percent traces of a compound of Eu with a Debye temperature of about 220°K and an isomer shift of about −1.15 cm/sec for the 21.7-keV transition are sufficient to explain the absorption spectrum of the 103-keV γ rays in Eu metal: The broad line obtained is composed of two lines of approximately equal in-

TABLE I. Isomer shifts in europium compounds (cm/sec).

Line / Compound	21.7 keV	97 keV	103 keV
$EuAl_2$	$-0.97(3)^a$	0.93(5)	1.03(3)
$EuAl_4$	$-1.14(3)^a$	1.27(6)	1.33(4)
$EuCu_2$	$-0.88(3)^a$	0.90(5)	0.98(4)
$EuPt_2$	$-0.95(4)^a$	0.94(6)	1.04(8)
$EuRh_2$	$0.20(5)^b$	−0.18(6)	−0.21(5)
$EuPd_3$	$0.35(3)^b$	−0.31(4)	−0.40(3)
$EuSO_4$	$-1.5\ (1)^c$	$1.53(15)^c$	$1.8\ (1)^c$
Eu	$-0.78(1)^d$		

[a] Reference 8.
[b] Reference 9.
[c] Reference 12.
[d] Reference 15.

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[15] P. Brix, S. Hüfner, P. Kienle, and D. Quitman, Phys. Letters **13**, 140 (1964).

TABLE II. Summary of results obtained with the 97-keV γ Rays of Eu^{153} at 20°K.

Compound	Amount of Eu (mg/cm^2)	Effect (%)	t	(%)	θ (°K)	Γ_m (mm/sec)	Γ_a (mm/sec)
$EuAl_2$	230	2.7	3.2	3.7	190±10	19.5	6.8±1.0
$EuAl_4$	120	1.4	0.9	2.0	160±10	14.0	5.8±1.0
$EuRh_2$	90	2.0	1.6	4.7	205±10	18.0	7.2±1.0
$EuCu_2$	115	1.5	1.05	2.4	170±10	15.0	6.5±1.0
EuPt	57	1.4	0.95	4.4	200±10	15.0	6.6±1.0
$EuPd_3$	105	2.0	1.6	4.0	195±10	14.0	5.7±1.0
Eu_2O_3	180	3.3	4.8	7.0	225±10	18.5	5.6±1.0
Average:							6.3±0.4
Eu	650	1.2	0.8	0.32		18.2	(8.7±1.0)

tensities—one resulting from the impurities and the other from the Eu metal itself.

The Debye temperatures of all the compounds investigated were deduced from the absorption spectra observed, assuming the validity of the Debye-Waller formula[11] for these intermetallic compounds. The absorption measurements of the 97-keV γ rays are very suitable for studies of Mössbauer-effect efficiencies. Because of the short lifetime[12] of the 97-keV level $[\tau_{1/2}=(2.14\pm0.2)\times(10^{-10}$ sec$]$, and because of the weakness of the hyperfine interaction in the intermetallic compounds of Eu at 20°K (as determined from the absorption measurements of the 21.7-keV γ rays of Eu^{151}), the broadenings of the 97-keV absorption lines are due only to the finite absorber thicknesses. In such cases, N—the height of the absorption peak corrected for background—is given by[16]

$$N=f_s[1-e^{-t/2}Y_0(it/2)], \tag{2}$$

where $t=n\sigma f_a$ and $Y_0(x)$ is the Bessel function of zero order. Here f_s and f_a are the probabilities for recoilless emission and absorption, respectively, n is the number of Eu^{153} nuclei in 1 cm^3 of the absorber, and $\sigma=\sigma_0/(1+\alpha)$. Using Eq. (2) and assuming that f_s for an oxide source is equal to the value of f_a of an oxide absorber, the value of f_s could be derived. Once f_s is known, the values of t for the various absorbers could be obtained and from them the values of f_a were derived. The results obtained for the Mössbauer-effect efficiencies and for the Debye temperatures—using the Debye-Waller relation—of are summarized in Table II. It is seen that the values Θ_D are lower than the value of Θ_D for Eu_2O_3 and are in a range between 160 and 200°K. A similar result was obtained previously for Θ_D of Tb in $TbAl_2$ (170±10°K).[17] The measured and true half-widths of the absorption lines of the 97-keV radiation (Γ_m and Γ_a) are also given in Table II. The values of Γ_a were derived from those of Γ_m by using the relation $\Gamma_m=\Gamma_a(2+0.27t)$.[18] All the values of Γ_a, except that calculated from the Eu metal absorption line, are in agreement with each other and with the values determined previously from measurements with Eu_2O_3 and $EuSO_4$ absorbers.[6] The value deduced for Γ_a is (6.4±0.4) mm/sec, which corresponds to a half-life of $(2.2\pm0.4)\times10^{-10}$ sec for the 97-keV level. The large value obtained for Γ_a of the metallic Eu absorber provides an additional support to the hypothesis that the absorption line obtained with this absorber is partially produced by impurities.

All the absorption lines obtained for the 103-keV γ rays are broadened by hyperfine interactions. In $EuAl_2$, which is magnetically ordered at 20°K, the broadening factor ($\Gamma_m/2\Gamma_n$, where Γ_n is the natural width of the level) is about 4. All the other Eu intermetallic compounds are not magnetically ordered at 20°K, and the broadening factor found for them (and for Eu_2O_3) is about 2. It is difficult to derive accurate values of Mössbauer-effect efficiencies from the absorption spectra of the 103-keV γ rays because of the broadening produced by the hyperfine interactions. The values of Θ_D deduced from these spectra, taking into account the line broadenings, are in agreement with those derived from the measurements with the 97-keV γ rays.

The maximum effect obtained with the 650-mg/cm^2 metallic Eu absorber at 4°K, using the 103-keV γ rays of Eu^{153}, was 0.06% (see Fig. 5). Assuming that most of the absorption at the region indicated by the arrow in Fig. 5 corresponds to the metal itself, a value of $(1.06\pm0.4)\times10^{-3}$ is found for f_a of Eu metal (for 103-keV γ rays) at 4.2°K. This value of f corresponds to a Debye temperature of (94±6)°K. A value close to

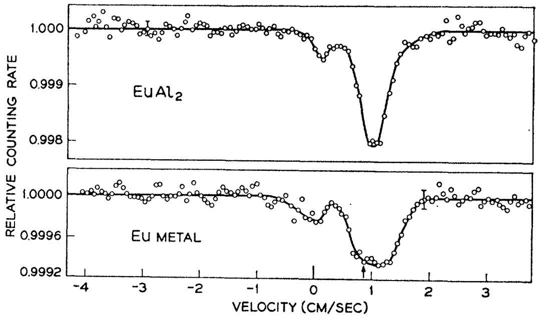

FIG. 5. The absorption of the 103-keV γ rays of Eu^{153} in $EuAl_2$ and Eu metal at 4.2°K as a function of relative velocity between source and absorber.

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[18] Ref. 11, p. 45.

this was estimated by Lounasmaa[19] by the extrapolation to 0°K of Debye temperatures at $T \geq 120°$K calculated by Nereson *et al.*[20] from neutron diffraction data.

CONCLUSIONS

The results of the measurements of the isomer shifts of the 21.7-keV γ rays of Eu^{151} and the 97 and 103-keV γ rays of Eu^{153} in various Eu compounds are consistent with the "conventional" theory, according to which ΔE can be expressed as a product of a nuclear factor and an electronic factor [Eq. (1)]. The anomaly observed for a metallic Eu absorber is very probably a result of the low Debye temperature of the metal and the existence of small amounts of impurities in the metal. Effects which could cause a breakdown of Eq. (1), such as different electron-wave distortions (due to the finite volume of the nucleus) for s and $p_{1/2}$ electrons or nuclear polarization effects not proportional to the total electron density at the nucleus, were not detected in the isomer-shift measurements.

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Field-Induced Resonance States at a Surface*†

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Observations of the field ionization of gases near a metal surface have shown the presence of a well-defined oscillating structure in the parent-ion energy distributions. The energy separations of the peaks in the structure are of the order of several volts. The separations increase with field. Peak positions are to first order independent of temperature and surface crystal orientation. The structure is interpreted in terms of resonant states formed by the combination of the externally applied field and the surface potential. Electrons from the ionizing gas atoms are partially reflected from the surface and interfere constructively to enhance the transmission into the metal for surface-to-atom separations corresponding to maxima in the observed distributions. The energy separations of the peaks are approximately given by the eigenvalues of a one-dimensional triangular well outlined by the electric field and surface. Numerical lifetime calculations, using one-dimensional macroscopic potentials appropriate to the case of field ionization, agree semiquantitatively with experiment.

I. INTRODUCTION

An isolated atom placed in an electric field will auto-ionize at a rate which increases rapidly with field.[1] The rate is experimentally appreciable only at fields large enough so that the drop in potential across the atom is of the same order as the ionization potential. Such fields ($\cong 10^8$ V/cm) are easily produced by sharpening the end of a metallic whisker or "tip" to a radius of a few hundred angstroms and charging it, in vacuum, to a positive potential of several kilovolts.[2] Introduction of gas to the system will lead to measurable ion current if the pressure and electric field are sufficiently high. A detailed description of the dynamics of the system is difficult since ionization rates depend, among other things, on diffusion rates of adsorbed layers, supply rates from the gas phase, and accommodation to the surface. Furthermore, the *a priori* ionization probability is a strong function of location with respect to the surface[3] because of the decrease in field with distance from the tip, and because of the structure of the surface. The effect of the latter is a primary concern of this paper.

The dependence of the ionization rate on position in directions tangential to the surface has been obtained through the use of the field ion microscope.[2] From the microscope patterns it appears that ionization occurs preferentially at sites directly above individual surface atoms. The ionization probability as a function of distance from the surface is susceptible to exploration by analysis of the kinetic energy of the ions after acceleration because the kinetic energy of an ion is related to the distance from the surface at which it was created. The high electric field enables resolution of distances of the order of a fraction of an angstrom. Although conceivably

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† Submitted to the Department of Physics, The University of Chicago in partial fulfillment of the requirements for the Ph.D. degree.

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