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## Hyperfine Structure in Trivalent Plutonium

N. Edelstein and R. Mehlhorn

Lawrence Radiation Laboratory, University of California, Berkeley, California 94720

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The hyperfine structure constants of  $\text{Pu}^{3+}$  in  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  are analyzed and the values  $\langle 1/r^3 \rangle = 7.57 \pm 0.57$  a.u. and  $a_{\text{Pu}^{3+}} = -(556 \pm 42) (g_J - 1) (\mu_N/I)$  Mc/sec are derived. Relativistic Dirac-Slater and Dirac-Fock wave functions give a value for  $\langle 1/r^3 \rangle$  about 9% lower than the empirical value. The core-polarization effect in the actinide ion  $\text{Pu}^{3+}$  is much larger than in the lanthanide series.

### I. INTRODUCTION

Values of the nuclear dipole moment of  $^{239}\text{Pu}$  derived from different types of measurements varied widely when the data were first analyzed. Subsequent analyses showed these results could be brought into agreement by a complete theoretical treatment including intermediate coupling and core-polarization effects.<sup>1</sup> Attempts to explain the sign of the core-polarization term with basis wave functions obtained from the central-field model of atomic structure proved inadequate until admixtures of continuum states were included.<sup>1</sup> Unfortunately, this type of calculation is very difficult. Exchange-polarized Hartree-Fock calculations were able to account for the sign and approximate magnitude of core-polarization effects<sup>2</sup> in the lanthanide series.

The electron-paramagnetic-resonance spectra of  $\text{Pu}^{3+}$ ,  $5f^5$ , have recently been measured in cubic symmetry sites in  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$ . The Zeeman-splitting factors ( $g$  values) have been interpreted by calculating the crystalline field mixing of the first excited  $J = \frac{7}{2}$  state with the ground  $J = \frac{5}{2}$  state.<sup>3</sup> In this paper we analyze the hfs data for  $\text{Pu}^{3+}$  in a similar manner, and use the known nuclear magnetic moment<sup>4</sup> of  $^{239}\text{Pu}$  to derive values for the core-polarization effect and  $\langle 1/r^3 \rangle$ . The latter quantity is compared with various theoretical calculations.

### II. THEORY AND RESULTS

#### A. Theoretical Summary

The nonrelativistic hyperfine Hamiltonian may be written as

$$\mathcal{H} = (2\beta\beta_N\mu_N/I) \left[ \sum_i (\vec{N}_i \cdot \vec{I}/r_i^3) + \frac{1}{3} 8\pi \sum_i \delta(\vec{r}_i) \vec{s}_i \cdot \vec{I} \right], \quad (1)$$

where  $\beta$  and  $\beta_N$  are the Bohr magneton and the nuclear magneton, respectively,  $\mu_N$  is the nuclear moment,  $I$  is the nuclear spin,  $\vec{r}_i$  is the radius vector for the  $i$ th electron, and  $\delta(\vec{r}_i)$  is the Dirac  $\delta$  function which is nonzero only for  $s$  electrons. The operator  $\vec{N}_i$  for the  $i$ th electron is written in terms of tensor operators as

$$\vec{N}_i = \vec{L}_i - (10)^{1/2} (\vec{s}^{(1)} \vec{C}^{(2)})^{(1)}_i, \quad (2)$$

where  $\vec{L}_i$  and  $\vec{s}_i$  are the orbital and spin angular momentum vectors and  $\vec{C}^{(2)}$  is a second-rank tensor.<sup>5</sup> The operator  $\vec{N}_i$  has nonzero matrix elements only for electrons with  $l > 0$ . In order to account for the effect of core polarization which produces a net unpairing of  $s$  electrons, the second term is included in Eq. (1). The angular transformation properties of this term are proportional to the operator  $\vec{s}_i$ . Relativistic effects also transform as  $\vec{s}_i$  and are not distinguishable from core polarization in our present experiments.

For convenience of calculation, we follow the procedure of Bordarier *et al.*,<sup>6</sup> and introduce the coupled double-tensor operator  $\vec{W}^{(u,k)K}$ . For a configuration of equivalent electrons,  $l^N$ , the hyperfine operators are defined as

$$\begin{aligned} \vec{I} &= \left[ \frac{1}{3} 2l(l+1)(2l+1) \right]^{1/2} \vec{W}^{(01)1}, \\ -10^{1/2} (\vec{s}^{(1)} \vec{C}^{(2)})^{(1)} &= \left( \frac{l(l+1)(2l+1)}{(2l-1)(2l+3)} \right)^{1/2} \vec{W}^{(12)1}, \\ \vec{s} &= \left[ \frac{1}{2} (2l+1) \right]^{1/2} \vec{W}^{(10)1}. \end{aligned} \quad (3)$$

A general computer program has been written to evaluate matrix elements of the  $\vec{W}^{(k,k)K}$  operators. The procedure followed is to calculate the angular matrix elements, parametrize the necessary radial integrals and core-polarization effects, and evaluate the parameters from the measured hyperfine data.

The tensor operators  $\vec{W}^{(k,k)K}$  arise naturally in the relativistic hfs formalism developed by Sandars and Beck.<sup>7</sup> They defined an effective operator representing the relativistic hyperfine Hamiltonian as

$$\vec{\mathcal{H}}_{\text{eff}} = a(10)\vec{W}^{(10)1} + a(01)\vec{W}^{(01)1} + a(12)\vec{W}^{(12)1}. \quad (4)$$

The expressions for the  $a(k, k)$  are given in Ref. 6 and define the necessary combinations of radial integrals, which may then be calculated from relativistic wave functions. Such a calculation will be described in a later section. For purposes of fitting our data, we combine Eqs. (3) and (4) into the most convenient form to parametrize the experimental results<sup>8</sup>

$$\begin{aligned} \vec{\mathcal{H}}_{\text{eff}} = & (2\beta\beta_N\mu_N/I) \sum_i \vec{1}_i \langle 1/r^3 \rangle_{01} \\ & - 10^{1/2} (\vec{s}^{(1)} \vec{C}^{(2)})_i^{(1)} \langle 1/r^3 \rangle_{12} + \vec{s}_i \langle 1/r^3 \rangle_{10} \}. \end{aligned} \quad (5)$$

In the nonrelativistic approximation (assuming no effects due to core polarization),  $\langle 1/r^3 \rangle_{01} = \langle 1/r^3 \rangle_{12}$  and  $\langle 1/r^3 \rangle_{10} = 0$ . For our calculations we shall assume the nonrelativistic approximation  $\langle 1/r^3 \rangle_{01} = \langle 1/r^3 \rangle_{12}$ , but because core-polarization and relativistic effects transform as  $\vec{s}$  we parametrize this operator.

#### B. Application to $\text{Pu}^{3+}$

The electronic configuration of  $\text{Pu}^{3+}$  outside the closed shells is  $5f^5$ . The optical spectrum was originally measured by Lämmermann and Conway<sup>9</sup> and the data were further refined by Conway and Rajnak.<sup>10</sup> We use the intermediate coupled wave functions given by Conway and Rajnak for our calculations. In the alkaline-earth fluorides, the ground state  $J = \frac{5}{2}$  and the first excited state  $J = \frac{7}{2}$  are strongly mixed by the crystalline-field interaction. We assume the effects of higher  $J$  levels are neg-

TABLE I. Spin-Hamiltonian parameters for trivalent Pu.

Ion	Matrix	$\phi$	$ g $ Measured	$ A $ ( $10^{-3} \text{ cm}^{-1}$ )
$\text{Pu}^{3+}$	$\text{CaF}_2$	$-15.1^\circ$	$1.297 \pm 0.002$	$6.72 \pm 0.06$
$\text{Pu}^{3+}$	$\text{SrF}_2$	$-13.2^\circ$	$1.250 \pm 0.002$	$8.46 \pm 0.1$
$\text{Pu}^{3+}$	$\text{BaF}_2$	$-11.0^\circ$	$1.187 \pm 0.004$	$10.2 \pm 0.3$

TABLE II. Truncated basis sets for the  $J = \frac{5}{2}$  and  $J = \frac{7}{2}$  levels. (Notation from Nielsen and Koster, Ref. 11.)

	$J = \frac{5}{2}$		$J = \frac{7}{2}$	
	Coef.	Coef. (%) (Ref. 2)	Coef.	Coef. (%) (Ref. 2)
$^6F$	0.1003	1.01	0.1037	1.07
$^6H$	0.8121	65.95	0.8951	80.12
$^4F3$	-0.1283	1.65	-0.1018	1.04
$^4G1$	-0.3097	9.59	-0.2451	6.01
$^4G3$	-0.1106	1.22	0.0677	0.45
$^4G4$	-0.3775	14.25	0.3053	9.33
	Total	93.67	Total	98.02

ligible. We obtain the amount of  $J$  mixing between the  $\frac{5}{2}$  and  $\frac{7}{2}$  states from the previous analysis of the Zeeman-splitting factors ( $g$  values).<sup>3</sup> The crystalline-field wave function is written as

$$\Gamma_7^1 = \cos\phi |J = \frac{5}{2}, \Gamma_7^*\rangle - \sin\phi |J = \frac{7}{2}, \Gamma_7^{*'}\rangle,$$

where the crystalline-field wave functions  $\Gamma_7^*$  and  $\Gamma_7^{*'}$  are the same as defined previously. In Table I we list the pertinent results taken from our earlier work.

The hyperfine Hamiltonian can be evaluated by summing matrix elements of the type

$$\langle \Gamma_7^1 | \vec{W}^{(k,k)K} | \Gamma_7^1 \rangle,$$

and multiplying by the appropriate factors given in Eq. (3). For the  $J = \frac{5}{2}$  level, the complete intermediate coupled wave function consists of a linear combination of 28  $LS$  states and the  $J = \frac{7}{2}$  level consists of a linear combination of 30  $LS$  states. In calculating matrix elements of the Zeeman operator for our earlier paper, we obtained matrix elements of the operators  $\Sigma \vec{1}_i$  and  $\Sigma \vec{s}_i$  for the complete basis sets. The complexity of the operator  $(\vec{s}^{(1)} \vec{C}^{(2)})_i^{(1)}$  obliged us to work with a truncated basis set in computing its matrix elements. The operators  $\Sigma \vec{1}_i$  and  $\Sigma \vec{s}_i$  were recomputed with the truncated basis sets in order to provide some estimate of the effects of truncation. The truncated basis sets are given in Table II. The notation is from Nielsen and Koster.<sup>11</sup>

For each operator  $\vec{O}$  in the hyperfine Hamiltonian, the matrix elements are

$$\begin{aligned} \langle \Gamma_7^1 | \Sigma \vec{O}_i | \Gamma_7^1 \rangle = & \langle J = \frac{5}{2}, \Gamma_7^* | \Sigma \vec{O}_i | J = \frac{5}{2}, \Gamma_7^* \rangle \cos^2\phi \\ & - 2 \langle J = \frac{5}{2}, \Gamma_7^* | \Sigma \vec{O}_i | J = \frac{7}{2}, \Gamma_7^{*'} \rangle \sin\phi \cos\phi \\ & + \langle J = \frac{7}{2}, \Gamma_7^{*'} | \Sigma \vec{O}_i | J = \frac{7}{2}, \Gamma_7^{*'} \rangle \sin^2\phi, \end{aligned} \quad (6)$$

where  $\vec{O}_i$  is  $\vec{1}_i$ ,  $-10^{1/2}(\vec{s}^{(1)} \vec{C}^{(2)})_i^{(1)}$ , or  $\vec{s}_i$ . The angle  $\phi$  is obtained by the previous fit to the  $g$  values.

TABLE III. Numerical values of the general hyperfine matrix elements for trivalent Pu in cubic symmetry.

$\Sigma \vec{O}_i$	Truncated	Complete	$\Sigma \vec{I}_i$	$\Sigma -10^{1/2}(\vec{s}^{(1)}\vec{C}^{(2)})_i^{(1)}$	$\Sigma \vec{s}_i$
			Truncated	Truncated	Complete
$\langle J=\frac{5}{2}, \Gamma_7^+   \Sigma \vec{O}_i   J=\frac{5}{2}, \Gamma_7^+ \rangle$	-1.259	-1.317	0.090	0.479	0.483
$2 \langle J=\frac{5}{2}, \Gamma_7^+   \Sigma \vec{O}_i   J=\frac{7}{2}, \Gamma_7^+ \rangle$	1.603	1.627	-0.068	-1.603	-1.627
$\langle J=\frac{7}{2}, \Gamma_7^+   \Sigma \vec{O}_i   J=\frac{7}{2}, \Gamma_7^+ \rangle$	1.674	1.703	-0.116	-0.204	-0.203

In Table III we give the value for the matrix elements shown in Eq. (6). We then evaluate Eq. (6) for the values of  $\phi$  given in Table I with the results shown in Table IV.

The hfs constant may now be written (in the non-relativistic approximation) as

$$A = A_f + A_c,$$

where

$$A_f = \theta [\langle \Gamma_7^+ | \Sigma \vec{I}_i | \Gamma_7^+ \rangle + \langle \Gamma_7^+ | \Sigma -10^{1/2}(\vec{s}^{(1)}\vec{C}^{(2)})_i^{(1)} | \Gamma_7^+ \rangle],$$

$$A_c = C \langle \Gamma_7^+ | \Sigma \vec{s}_i | \Gamma_7^+ \rangle, \quad (7)$$

and

$$\theta = (4\beta\beta_N\mu_N/I) \langle 1/r^3 \rangle.$$

$C$  is a parameter which is proportional to  $\mu_N/I$  and gives the contribution due to core polarization. We have used the  $\text{CaF}_2$  and  $\text{SrF}_2$  matrix elements in Table IV to obtain the parameters and then used the  $\text{BaF}_2$  result as a check because the accuracy of the measurements in the first two crystals is greater than for  $\text{BaF}_2$ . The results are  $\theta = 0.00981 \text{ cm}^{-1}$ ,  $C = -0.0147 \text{ cm}^{-1}$ . The signs of the experimental values of  $A$  are unknown. In order to obtain consistent results, they are chosen as negative. This choice is necessary because  $\mu_N$  of  $^{239}\text{Pu}$  is positive and thus  $\theta$  must be positive.

Because we wish to compare our values with those from atomic-beam and optical-spectroscopy experiments, we now calculate the hyperfine parameters for a pure  $J=\frac{5}{2}$  and a  $J=\frac{7}{2}$  state. We use the matrix elements given in Table III for the pure

states and the parameters just evaluated. The results are given in Table V. In order to obtain the data for a free ion, we have made use of the relationship  $g_J/a = g/A$ , where  $g_J$  and  $a$  are the Landé  $g$  value and hyperfine coupling constant for a free ion.<sup>12</sup> The hyperfine coupling constant for a free ion is also the sum of two terms similar to Eq. (7):

$$a = a_f + a_c.$$

We also list in Table V values for  $a_c$  and  $a_f$ .

The core-polarization term may be written<sup>13</sup>

$$a_c = (g_J - 1)K(\mu_N/I),$$

where

$$K = C(I/\mu_N). \quad (8)$$

The term  $(g_J - 1)$  is the value of the angular matrix element of the operator  $\Sigma \vec{s}_i$  for a pure  $J$  state. From our values of  $a_c$ , we find

$$a_c = -(556 \pm 42)(g_J - 1)(\mu_N/I) \text{ Mc/sec} \quad (9)$$

for the  $\text{Pu}^{3+}$  free ion. From  $\theta$  we calculate

$$\langle 1/r^3 \rangle_{\text{Pu}^{3+}} = 7.57 \pm 0.57 \text{ a.u.}$$

The errors in our parameters are estimated in the following way. From the uncertainty in the experimental data, the maximum error is 2%. There is also a 2% uncertainty in the value of  $\mu_N$  of  $^{239}\text{Pu}$ . If we assume the error due to truncation of the basis set for the operator  $\Sigma -10^{1/2}(\vec{s}^{(1)}\vec{C}^{(2)})_i^{(1)}$  is the same as for the operator  $\Sigma \vec{I}_i$ , then considering the relative magnitudes of the matrix elements, the truncation error is about 0.7% of the total value

TABLE IV. Numerical values of the hyperfine matrix elements of trivalent Pu for the alkaline-earth fluorides.

		$\Sigma \vec{I}_i$		$\Sigma -10^{1/2}(\vec{s}^{(1)}\vec{C}^{(2)})_i^{(1)}$	$\Sigma \vec{s}_i$		$2\Sigma(\vec{I}_i + 2\vec{s}_i)$
	$\phi$	Truncated	Complete		Truncated	Complete	Complete
CaF <sub>2</sub>	-15.1°	-0.657	-0.703	0.059	0.030	0.028	-1.294
SrF <sub>2</sub>	-13.2°	-0.750	-0.798	0.064	0.087	0.086	-1.252
BaF <sub>2</sub>	-11.0°	-0.852	-0.902	0.070	0.154	0.154	-1.188
			$\Sigma \vec{N}_i = \Sigma[\vec{I}_i \text{ (comp)} - 10^{1/2}(\vec{s}^{(1)}\vec{C}^{(2)})_i^{(1)}]$				
CaF <sub>2</sub>			-0.644				
SrF <sub>2</sub>			-0.733				
BaF <sub>2</sub>			-0.832				

TABLE V. Extrapolated hyperfine parameters for pure  $J=\frac{5}{2}$  and  $J=\frac{7}{2}$  states of  $\text{Pu}^{3+}$  in a cubic crystalline field and as a free ion.

	$A$	$A_f$ ( $10^{-3} \text{ cm}^{-1}$ )	$A_c$	$a$	$a_f$ ( $10^{-3} \text{ cm}^{-1}$ )	$a_c$	$g_J$
$J=\frac{5}{2}$	-19.19	-12.02	-7.16	11.51	7.21	4.30	0.420
$J=\frac{7}{2}$	18.55	15.55	3.00	6.18	5.18	1.00	0.865

of the matrix element of the operator  $\Sigma \vec{N}_i$ . In the next section we show the error due to the assumption  $\langle 1/r^3 \rangle_{01} = \langle 1/r^3 \rangle_{12}$  is negligible. The largest error probably is due to the neglect of higher  $J$  levels mixed in by the crystalline field. We have given the parameters an error of  $\pm 7.5\%$  which we believe is a conservative estimate.

### III. DISCUSSION

Recently there have been relativistic calculations for the elements and some ions through the actinide series. Mann from Los Alamos Scientific Laboratory (LASL) has sent us the wave functions for the 5f electrons of Pu I and Pu IV (spectroscopic notation) obtained from his Dirac-Fock calculations,<sup>14</sup> and Cromer, also from LASL, has sent us the wave functions obtained from Dirac-Slater calculations.<sup>15</sup> We have integrated these wave functions according to the definitions given by Bourdrier *et al.*<sup>6</sup> and the results are given in Table VI. In order to compare our experimental result with their wave functions we define

$$\Delta = \langle 1/r^3 \rangle_{12} - \langle 1/r^3 \rangle_{01} \quad (10)$$

Then we may write

$$\begin{aligned} A_f = & (4\beta\beta_N\mu_N/I) \langle 1/r^3 \rangle_{01} \langle \Gamma_7^1 | \Sigma \vec{I}_i | \Gamma_7^1 \rangle \\ & + (4\beta\beta_N\mu_N/I) (\Delta + \langle 1/r^3 \rangle_{01}) \\ & \times \langle \Gamma_7^1 | \Sigma - 10^{1/2} (\vec{S}^{(1)} \vec{C}^{(2)})_i^{(2)} | \Gamma_7^1 \rangle. \end{aligned}$$

The percentage correction to the  $\langle 1/r^3 \rangle_{01}$  of Table VI by our assumption that  $\langle 1/r^3 \rangle_{01} = \langle 1/r^3 \rangle_{12}$  in our analysis is

$$\frac{\Delta \langle \Gamma_7^1 | \Sigma - 10^{1/2} (\vec{S}^{(1)} \vec{C}^{(2)})_i^{(2)} | \Gamma_7^1 \rangle}{\langle 1/r^3 \rangle_{01} \langle \Gamma_7^1 | \Sigma \vec{N}_i | \Gamma_7^1 \rangle} \times 100 \sim -0.3\% \quad (11)$$

using data from Tables IV and VI. The corrected values are also given in Table VI. Comparison of the theoretical  $\langle 1/r^3 \rangle_{01}$  and the experimental  $\langle 1/r^3 \rangle$  gives a discrepancy of 9%. There is essentially no difference between the Dirac-Fock and the

Dirac-Slater calculations for the  $\langle 1/r^3 \rangle$  integrals.

The magnitude of the core-polarization effect is much larger than found for rare-earth ions. Bleaney<sup>16</sup> has shown that for the  $\text{Eu}^{2+}$

$$a_{c_{\text{Eu}^{2+}}} = -(63 \pm 10) (g_J - 1) (\mu_N/I) \text{ Mc/sec} \quad (12)$$

He assumed that this equation was valid throughout the 4f transition series but recent experimental and theoretical work questions this assumption.<sup>2,12</sup>

The core-polarization effect in  $\text{Pu}^{3+}$  [Eq. (9)] is almost an order of magnitude larger than found for  $\text{Eu}^{2+}$  in the lanthanide series. Our value for  $\text{Pu}^{3+}$  is slightly larger than the core-polarization effect derived by Easley<sup>17</sup> for  $\text{Am}^{2+}$ :

$$a_{c_{\text{Am}^{2+}}} = -(420 \pm 42) (g_J - 1) (\mu_N/I) \text{ Mc/sec} \quad (13)$$

but corroborates the magnitude of the effect.

Bauche and Judd<sup>1</sup> and Armstrong and Marrus<sup>18</sup> have shown that the equation

$$a_{c_{\text{atoms}}} = -(70 \pm 20) (g_J - 1) (\mu_N/I) \text{ Mc/sec} \quad (14)$$

is consistent with the interpretation of the data for Pu I ( $5f^6 7s^2$ ) and Am I ( $5f^7 7s^2$ ). From the values of  $\langle 1/r^3 \rangle_{10}$  given in Table VI the equation

$$a_{\text{rel}} = -(67 \pm 10) (\mu_N/I) (g_J - 1) \text{ Mc/sec} \quad (15)$$

may be obtained. These calculations show relativistic effects for the atoms and ions are approximately equal and agree well with the empirical equation for the actinide atoms Pu I and Am I. The core-polarization effects in the ions Pu IV and Am III are about seven times larger than relativistic effects in actinide atoms. Because of the agreement found for the calculated  $\langle 1/r^3 \rangle_{01}$  with the experimental value the relativistic Dirac-Fock and Dirac-Slater calculations probably give the right magnitude for relativistic effects in the heavy atoms. Therefore it appears that  $a_{c_{\text{atoms}}}$  [Eq. (14)] is mostly due to relativistic effects, and that in the ions where there are no 7s electrons there are very large core-polarization effects.

TABLE VI. Calculated values for the radial parameters using relativistic wave functions.

	$\langle 1/r^3 \rangle_{01}$ (a.u.)	$\langle 1/r^3 \rangle_{01}(\text{corr.})$ (a.u.)	$\langle 1/r^3 \rangle_{12}$ (a.u.)	$\langle 1/r^3 \rangle_{10}$ (a.u.)
$f^6 s^2 \text{ Pu I DS}$	6.092		7.594	-0.706
$f^5 \text{ Pu IV DS}$	6.879	6.86	8.166	-0.595
$f^6 s^2 \text{ Pu I DF}$	6.184		7.849	-0.788
$f^5 \text{ Pu IV DF}$	6.936	6.92	8.308	-0.639

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## Recoilless Fraction in Microcrystals\*

R. Ruppin†

Department of Physics, University of North Carolina, Chapel Hill, North Carolina 27514  
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The recoilless fraction  $f$  in monoatomic microcrystals is calculated from a lattice-dynamical model. Its dependence on the physical boundary conditions at the surfaces of the crystal-lites is shown to follow the rule that  $f$  increases with increasing stiffness of the binding to the surrounding medium. A modified form of the Debye approximation, which has been used in the past to explain Mössbauer-effect experiments on microcrystals, is found to yield results which are incompatible with those derived from lattice dynamics. The reasons for the failure of the Debye approximation to predict the recoilless fraction in microcrystals are discussed.

## I. INTRODUCTION

In experimental studies of the Mössbauer effect in microcrystals the recoilless fraction  $f$  was found to differ from the corresponding fraction  $f_\infty$  of macroscopic samples.<sup>1-3</sup> No obvious common trend emerged when the results obtained on different crystals were compared. In tin<sup>2</sup> and tungsten<sup>3</sup> microcrystals,  $f$  was observed to be smaller than  $f_\infty$ , while in gold<sup>1</sup> microcrystals  $f$  was found to be larger than  $f_\infty$ . In theoretical discussions of this effect the Debye model was employed,<sup>1,3-5</sup> but with the frequency spectrum modified to account for the smallness of the samples. This subject,

as well as many other aspects of the Mössbauer effect in microcrystals, has recently been reviewed by Schroeder.<sup>6</sup>

The related problem of the Debye-Waller factor for surface atoms of large crystals has been investigated experimentally by low-energy electron diffraction. These experiments and the lattice-dynamical calculations which have been performed in order to explain their results have been reviewed by Maradudin<sup>7</sup> in 1966. More recent LEED work, in which the Debye-Waller factors of surface atoms were measured, was reported by Jones, McKinney, and Webb,<sup>8</sup> by Goodman, Farrell, and Somorjai,<sup>9</sup> and by Morabito, Steiger, and Somorjai.<sup>10</sup> Further