ACKNOWLEDGMENTS

We wish to thank Dr. D. T. Cromer and Dr. J. B. Mann for sending us the wave functions obtained from their calculations, and Dr. W. B. Lewis and Dr. J. B. Mann for helpful discussions.

*Work supported under the auspices of the U. S. Atomic Energy Commission.

[1]J. Bauche and B. R. Judd, Proc. Phys. Soc. (London) 83, 145 (1964); and references therein.

[2]A. Freeman, in *Hyperfine Structure and Nuclear Radiations*, edited by E. Matthias and D. A. Shirley (North-Holland, Amsterdam, 1968), p. 427.

[3]N. Edelstein, H. F. Mollet, W. C. Easley, and R. J. Mehlhorn, J. Chem. Phys. 51, 3281 (1969).

[4]J. Faust, R. Marrus, and W. A. Nierenberg, Phys. Letters 16, 71 (1965).

[5]B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill, New York, 1963).

[6]Y. Bordarier, B. R. Judd, and M. Klapisch, Proc. Roy. Soc. (London) A289, 81 (1965).

[7]P. G. H. Sandars and J. Beck, Proc. Roy. Soc. (London) A289, 97 (1965).

[8]We have briefly outlined the pertinent equations necessary to evaluate our data. For a complete discussion of relativistic hyperfine theory see Refs. 6 and 7.

[9]H. Lämmerman and J. G. Conway, J. Chem. Phys. 48, 259 (1963).

[10]J. G. Conway and K. Rajnak, J. Chem. Phys. 44, 348 (1966).

[11]C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^n, d^n, f^n Configurations* (Technology Press, Cambridge, Mass., 1963).

[12]B. Bleaney, in *Hyperfine Interactions*, edited by A. Freeman and R. Frankel (Academic, New York, 1967), p. 1.

[13]For a more detailed discussion of core polarization see Ref. 1.

[14]J. Mann (private communication).

[15]D. Liberman, J. T. Waber, and D. T. Cromer, Phys. Rev. 137, A27 (1965).

[16]B. Bleaney, in *Proceedings of the Third International Conference on Quantum Electronics* (Columbia U. P., New York, 1964).

[17]W. C. Easley, UCRL Report No. UCRL-17699, 1967 (unpublished).

[18]L. Armstrong, Jr., and R. Marrus, Phys. Rev. 144, 994 (1966).

PHYSICAL REVIEW B VOLUME 2, NUMBER 5 1 SEPTEMBER 1970

Recoilless Fraction in Microcrystals*

R. Ruppin †

Department of Physics, University of North Carolina, Chapel Hill, North Carolina 27514

(Received 10 April 1970)

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 crystallites 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_∞ of macroscopic samples.[1-3] No obvious common trend emerged when the results obtained on different crystals were compared. In tin[2] and tungsten[3] microcrystals, f was observed to be smaller than f_∞, while in gold[1] microcrystals f was found to be larger than f_∞. In theoretical discussions of this effect the Debye model was employed,[1,3-5] 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 Schroeer.[6]

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[7] in 1966. More recent LEED work, in which the Debye-Waller factors of surface atoms were measured, was reported by Jones, McKinney, and Webb,[8] by Goodman, Farrell, and Somorjai,[9] and by Morabito, Steiger, and Somorjai.[10] Further

theoretical discussions have been given by Wallis, Clark, and Herman,[11] by Wallis, Clark, Herman and Gazis,[12] and by Corciovei, Grecu, and Radescu.[13] The theoretical results for surface atoms on macrocrystals are not directly applicable to microcrystals since they are all subject to two limitations. First, the crystals were assumed to be semi-infinite whereas for microcrystals the effects due to the presence of a number of surfaces may interfere. Second, the calculations referred to free surfaces whereas in the case of microcrystals the binding to the surrounding medium can be of importance. The latter point has been emphasized by Van Wieringen[14] who demonstrated experimentally that the recoil-free fraction of iron oxide microcrystals depended on the degree of their coupling to the medium in which they were embedded.

In the present work lattice-dynamical calculations are performed for crystals with all dimensions small and for different boundary conditions at the surfaces. The lattice is assumed to be simple cubic and to have the shape of a cube with N atoms along each side. For a general force model the solution of the dynamical problem would require us to find the eigenvalues of a $3N^3 \times 3N^3$ system, which would be impracticable even for N as small as 5. This difficulty can be overcome only by choosing a simple model. It has been shown by Kothari and Singal[15] that if the Montroll-Potts model[16] is employed, the problem is reducible to that of a linear chain of N atoms. In this model the atoms are assumed to interact through nearest-neighbor central and noncentral forces but the x, y, and z components of displacements are uncoupled. Because of its simplicity this model has often been used, e. g., in the theory of defect modes,[16,17] of the infrared absorption due to impurities,[18] of the Mössbauer effect for an impurity atom,[19] and of the recoilless fraction of surface atoms on large crystals.[20] This model has, of course, some physically unrealistic features[7,17] and cannot reproduce the individual eigenfrequencies and polarization vectors of real crystals. It can, however, yield reasonable estimates for the Debye-Waller factor (which is not sensitive to the details of the normal-mode properties) and its behavior as a function of the size of the crystal and of the boundary conditions.

The results of our calculations are found to be incompatible with those derived from the modified Debye approximation. This approximation can yield results which are even qualitatively incorrect. The failure of the Debye model is shown to originate from some assumptions which are implicitly involved in it and which are invalid for small samples but do hold for large crystals.

The solutions for the linear chain, which will later serve as a basis for the solutions in three dimensions, are discussed in Sec. II. The recoilless fraction for the three-dimensional case is considered in Sec. III, where the lattice-dynamical and Debye-type approaches are compared. In Sec. IV the results of some numerical calculations are presented and compared with experimental data.

II. LINEAR CHAIN

Consider a linear chain consisting of N atoms of mass M. With nearest-neighbor interactions the equations of motion are

$$M\omega^2 u_l = \alpha(2u_l - u_{l-1} - u_{l+1}), \quad l = 2, 3, \ldots, N-1, \tag{1}$$

where u_l is the displacement of the atom l from equilibrium and α is the force constant. The equations of motion for the two end atoms, $l = 1$ and $l = N$, will be treated separately since they depend on the physical boundary conditions of which four different types will be discussed. The first three are well known and we will only write down the appropriate solutions. In the fourth case perturbed force constants are introduced for the end atoms and the solutions will be obtained by using the Green's-function method.

(*a*) *Fixed ends.* Here $u_1 = u_N = 0$ and the frequencies and the normalized eigenvectors are given by

$$\omega_m^2 = (4\alpha/M)\sin^2[m\pi/2(N-1)], \tag{2}$$

$$B(m, l) = [2/(N-1)]^{1/2}\sin[(l-1)m\pi/(N-1)], \tag{3}$$

where

$$m = 1, 2, \ldots, N-2.$$

(*b*) *Ends connected to rigid walls.* Here we assume that Eq. (1) holds also for $l = 1$, N and require $u_0 = u_{N+1} = 0$. Physically this means that the end atoms are connected to rigid walls with springs of force constant α. The choice of this force constant as being equal to the interatomic force constants simplifies the mathematical treatment but is, of course, arbitrary. This type of boundary condition is, nevertheless, important in that it represents an intermediate case between the two extreme (and more often discussed) cases of fixed and free ends. The solutions are given by

$$\omega_m^2 = (4\alpha/M)\sin^2[m\pi/2(N+1)], \tag{4}$$

$$B(m, l) = [2/(N+1)]^{1/2}\sin[lm\pi/(N+1)], \tag{5}$$

where

$$m = 1, 2, \ldots, N.$$

(*c*) *Free ends.* This can be expressed mathematically by assuming that Eq. (1) holds for the end atoms and by requiring that $u_0 = u_1$ and $u_{N+1} = u_N$.

The solutions are given by

$$\omega_m^2 = (4\alpha/M)\sin^2(m\pi/2N)\, m = 0, 1, \ldots, N-1 \quad (6)$$

$$B(m, l) = (2/N)^{1/2}\cos[(2l-1)m\pi/2N]$$
$$m = 1, 2, \ldots, N-1$$
$$= (1/N)^{1/2}, \quad m = 0 \quad (7)$$

(*d*) *Free ends and modified force constants for the end atoms.* Such models have been employed for semi-infinite crystals.[11,12] The changes in the force constants of surface atoms can occur due to the fact that these atoms have equilibrium positions which are different from those of bulk atoms[21,22] (i.e., there occur deviations from the bulk lattice constant). The equations of motion are the same as in (*c*) except that now the force constants connecting the end atoms to their neighbors, which will be denoted α', are different from all other force constants. In terms of the Green's functions [23]

$$g_{lk} = \sum_m [B(m, l)B(m, k)/(\omega^2 - \omega_m^2)] \quad (8)$$

of the unperturbed chain with free ends we obtain a set of four linear homogeneous equations for u_1, u_2, u_{N-1}, u_N. Utilizing the symmetry of the chain about its center, which is not disturbed by the perturbation, these reduce to the following two equations:

$$u_1 = 2\Delta(g_{11} - g_{12})(u_1 - u_2), \quad (9)$$

$$u_2 = 2\Delta(g_{12} - g_{22})(u_1 - u_2), \quad (10)$$

where $\Delta = (\alpha' - \alpha)/M$.

This yields the equation for the perturbed frequencies

$$2\Delta(g_{11} + g_{22} - 2g_{12}) = 1. \quad (11)$$

The displacements of the inner atoms are given in terms of those of the two end atoms by

$$u_l = 2\Delta(g_{l1} - g_{l2})(u_1 - u_2). \quad (12)$$

In the Green's functions appearing in Eqs. (9)–(12) the summation over m [Eq. (8)] is to be taken over either odd or even values only, according to whether perturbed modes of odd or even symmetry about the center are treated. We define ω_m to be the solution of Eq. (11) which coincides in the limit $\alpha' \to \alpha$ with the unperturbed frequency given by Eq. (6). We again denote the normalized eigenvectors by $B(m, l)$.

We define $\epsilon = (\alpha' - \alpha)/\alpha$ and note that for negative ϵ, i.e., softening of the forces at the ends of the chain, all frequencies (except for the zero frequency) are lowered. For positive ϵ all frequencies are raised and localized surface modes, whose frequencies lie above the maximum frequency of the unperturbed chain, can occur. The case of a semi-infinite chain with a modified force constant at the free end has been treated analytically[24,25] and it has been found that a surface mode occurs if $\epsilon > \frac{1}{3}$. For a finite chain two surface modes are possible. As the chain becomes very long these will become degenerate in frequency, being simply odd and even combinations of the surface modes of the semi-infinite chain.

III. RECOILLESS FRACTION

The recoilless fraction is

$$f = e^{-2W}, \quad (13)$$

where the Debye-Waller factor is given by

$$2W = \langle[\vec{k}\cdot\vec{u}(l)]^2\rangle . \quad (14)$$

Here $\vec{k}$ is the wave vector of the γ ray and the angular brackets denote a statistical average. The usual way to evaluate this is to perform a normal-coordinate transformation[23]

$$u_\alpha(l) = (\hbar/2M)^{1/2}\sum_m [B_\alpha(m, l)/(\omega_m)^{1/2}](b_m + b_m^\dagger), \quad (15)$$

where $\vec{B}(m, l)$ are the normalized eigenvectors of the dynamical matrix and $b_m^\dagger$ and b_m are the phonon-creation and -annihilation operators. The Debye-Waller factor then becomes

$$2W = (\hbar/2M)\sum_m \langle[\vec{k}\cdot\vec{B}(m, l)]^2\rangle[(2n_m + 1)/\omega_m], \quad (16)$$

where

$$n_m = \langle b_m^\dagger b_m\rangle = 1/[\exp(\beta\hbar\omega_m) - 1], \quad \beta = 1/kT. \quad (17)$$

For macroscopic crystals of cubic symmetry the following two assumptions are acceptable: (a) All atoms are dynamically equivalent, i. e., the mean-square displacement $\langle[u(l)]^2\rangle$ is independent of l; (b) each atom is located at a site of cubic symmetry, i. e., the mean-square displacements are isotropic, $\langle u_x^2\rangle = \langle u_y^2\rangle = \langle u_z^2\rangle$.

We note that these assumptions are inapplicable in the case of microcrystals, where the mean-square displacements will in general differ from atom to atom and will also be anisotropic.

If the two assumptions are valid, (16) reduces to

$$2W = \frac{R}{\hbar}\int_0^\infty \frac{N(\omega)}{\omega}\coth\left(\frac{\hbar\omega}{2kT}\right)d\omega, \quad (18)$$

where $R = \hbar^2k^2/2M$ is the recoil energy and $N(\omega)$ is the phonon density of states normalized to unity. If, furthermore, the Debye spectrum is used, as is usually done in discussions of experimental re-

sults, this becomes

$$2W=\frac{6R}{k\Theta_D}\left[\frac{1}{4}+\left(\frac{T}{\Theta_D}\right)^2\int_0^{\Theta_D/T}\frac{x\,dx}{e^x-1}\right], \tag{19}$$

where Θ_D is the Debye temperature.

Some previous attempts to interpret the results of experiments on microcrystals have been based on (18), but with a modified Debye spectrum so as to account for the smallness of the samples.[1,3-5] The main modification consisted of introducing, in addition to the short-wavelength cutoff Θ_D, also a long-wavelength cutoff Θ_L which depends on the dimensions of the crystal and on the physical boundary conditions at the surfaces. This cutoff is a manifestation of the fact that the wavelength of the longest elastic wave which can propagate in the crystal must be of the order of twice the largest dimension of the crystal. $N(\omega)$ was further modified by the addition of surface terms. Calculations based on this method[1,3] gave the result that f for a crystal with fixed surfaces is smaller than f for a crystal with free surfaces and that the latter is larger than f_∞ (except for very low temperatures[6]). Some of these conclusions are incorrect, as will be shown later in the lattice-dynamical treatment of the problem. The inadequateness of the modified Debye approximation is to be attributed to the failure of the two implicit assumptions (a) and (b) mentioned above.

To calculate f from the lattice-dynamical model we return to Eq. (16) and note that f depends on the atom l to which we are referring. Thus, assuming that all atoms have an equal probability of interacting with a γ ray, we define the recoilless fraction of the microcrystal to be an average of the recoilless fractions of the N^3 atoms.

In the Montroll-Potts model the equation of motion for the x component of the displacement of the atom at $l=(l_1, l_2, l_3)$ is

$$\begin{aligned}-M\omega^2x(l)&=\alpha_1[x(l_1-1,l_2,l_3)-2x(l)+x(l_1+1,l_2,l_3)]\\&+\alpha_2[x(l_1,l_2-1,l_3)-2x(l)+x(l_1,l_2+1,l_3)]\\&+\alpha_3[x(l_1,l_2,l_3-1)-2x(l)+x(l_1,l_2,l_3+1)],\end{aligned} \tag{20}$$

and the equations for the other components of displacement follow by symmetry. The normalized solutions of (20) are

$$B_x(m,l)=B(m_1,l_1)B(m_2,l_2)B(m_3,l_3), \tag{21}$$

where $m=(m_1, m_2, m_3)$ and $B(m_i, l_i)$ are the solutions of the corresponding one-dimensional problem defined in Sec. II. The eigenfrequencies are given by

$$\omega_m^2=(4/M)(\alpha_1\omega_{m_1}^2+\alpha_2\omega_{m_2}^2+\alpha_3\omega_{m_3}^2), \tag{22}$$

where ω_{m_i} are the frequencies given in Sec. II.

Since in our lattice-dynamical model the motions in the x, y, and z directions are independent and because the crystal as a whole has cubic symmetry, the recoilless fraction of the microcrystal cube is isotropic. We therefore may take $\vec{k}$ to be along the x axis, without loss of generality. We note, however, that the f of any individual atom will, in general, be anisotropic. The Debye-Waller factor of the microcrystal will be calculated by

$$2W=(R/\hbar N^3)\sum_{lm}[B_x(m,l)]^2[(2n_m+1)/\omega_m]. \tag{23}$$

IV. CALCULATIONS AND RESULTS

We have calculated f of cube-shaped microcrystals for the four types of boundary conditions discussed in Sec. II: (a) fixed boundaries; (b) surface atoms bound to a surrounding rigid medium by force constants which are equal to the interatomic force constants; (c) free boundaries; (d) free boundaries and modified force constants for the surface atoms.

In order to perform numerical calculations, a choice of the force constants α_i must be made. If the central and noncentral force constants are equal, as has been sometimes assumed for simplicity,[18-20] the mean-square displacements of surface atoms in directions parallel and perpendicular to the surface will be equal.[15,20] Since calculations for semi-infinite crystals based on more realistic models[26] show that the mean-square displacements of surface atoms in the direction perpendicular to the surface is larger than those in the parallel direction, and since physically the central force constants are expected to be considerably larger than the noncentral ones, we have chosen $\alpha_1=8\alpha_2=8\alpha_3$.

Since an experimental result for tungsten microcrystals is available[3] f was first calculated for the 46.5-keV Mössbauer transition of ^{183}W. We took $\alpha_1=1.43\times10^5$ dyne/cm which reproduces the experimental value of $f_\infty=0.61$ at 77 °K for macroscopic samples.[3] To calculate f_∞, the solutions of Eq. (20) with cyclic boundary conditions[16] were used. We disregard the fact that tungsten is not a simple-cubic crystal.

In Fig. 1 the ratio of f for a small cube to f_∞ is plotted as a function of the number of atoms along the edge of the cube. Curve (d) was calculated for $\epsilon=-0.5$, which is of the order of the changes expected in the force constants of surface atoms.[11] The relative positions of the four curves follow the general rule that f increases with increasing stiffness of the binding at the surfaces. Note that calculations based on the modified Debye approximation[3] predicted that curve (c) would be higher than curve (a). For all boundary conditions the recoil-

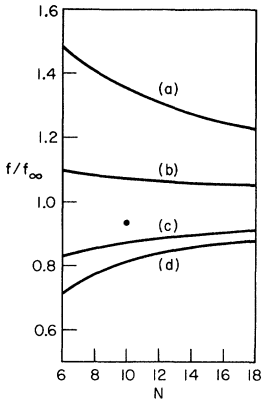

FIG. 1. Recoilless fraction for the 46.5-keV transition of ^{183}W in cube-shaped microcrystals. N is the number of atoms along the edge of the cube. Curve (a), fixed surfaces; curve (b), surface atoms bound to surrounding medium; curve (c), free surfaces; curve (d), free surfaces and smaller force constants for the surface atoms. The point corresponds to the experimental result of Roth and Hörl (Ref. 3).

less fraction tends to f_∞ with increasing N. The point in Fig. 1 corresponds to the experimental value $f = 0.57$ measured by Roth and Hörl[3] on tungsten microcrystals of diameter 30 Å in an organic embedding material. These crystallites contain about the same number of atoms as cubes with $N = 10$. Assuming that the change in f was caused by lattice-dynamical effects only, the position of the experimental point would indicate the existence of some degree of binding of the crystal to the surrounding medium (considerably weaker than the interatomic binding).

Marshall and Wilenzick[1] measured f in gold microcrystals and interpreted their results in terms of the modified Debye approximation. In order to obtain a curve which would fit the experimental results they found it necessary to assume for 60 Å microcrystals a Debye temperature which is higher than Θ_D of macroscopic samples. This change in the Debye temperature has been explained by Schroeer[27] as arising because of changes in the value of the lattice constant with decreasing crystal size. We note that this refers to changes which occur throughout the whole volume of the crystal. The change in the Debye temperature with a small change ΔV in the volume V of the unit cell is given by

$$\Theta_D' = (1 - \gamma \Delta V/V)^{-1} \Theta_D \,, \tag{24}$$

where γ is the Grüneisen constant. The change in volume can be incorporated into our lattice-dynamical model by assuming, in analogy with (24), that the force constant changes from its value α_1 in large crystals to

$$\alpha_1' = (1 - 2\gamma \Delta V/V)^{-1} \alpha_1 \,. \tag{25}$$

For gold the value $\alpha_1 = 4.25 \times 10^4$ dyne/cm was found to fit the experimental result measured on macrocrystals of $f = 0.177$ at 4.2 °K.[28] For 60-Å microcrystals the change in lattice constant was estimated from x-ray scattering data.[29] From (25), using the value $\gamma = 3.05$,[30] we obtain for the force constant of the 60-Å samples the value 4.62×10^4 dyne/cm. In Fig. 2 the recoilless fraction, as calculated from the lattice-dynamical model, is shown as a function of temperature. Curve II was calculated with cyclic boundary conditions and applies to macroscopic crystals. Curves I and III are for a cube with $N = 18$ (which contains about the same number of atoms as a 60-Å sphere) and with the change in force constant due to the decrease in lattice constant taken into account. Curve I is for free surfaces and curve III for surfaces connected to the surrounding medium with force constants equal to the interatomic ones. The open and dark circles correspond to experimental results on 60- and 200-Å gold microcrystals, respectively, which were embedded in gelatin. These data have been taken from a table given in Ref. 31. The data for the 200-Å samples follow quite closely the cal-

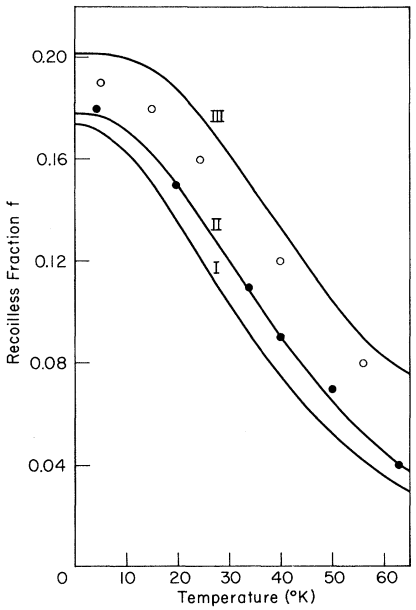

FIG. 2. Recoilless fraction for the Mössbauer transition of ^{197}Au. I: microcrystal cube ($N = 18$) with free surfaces; II: macroscopic crystal; III: microcrystal cube ($N = 18$) with surface atoms bound to the surrounding medium. The points correspond to the experimental data (Ref. 31) for 200-Å microcrystals (closed circles) and for 60-Å microcrystals (open circles).

culated macrocrystal curve. For this crystal size the deviations from f_∞ due to both lattice-dynamical and lattice-distortion effects are already very small. The data for the 60-Å microcrystals correspond, within our model, to some degree of binding (somewhat weaker than the interatomic binding) of the crystallites to the medium. The conclusion drawn from the modified Debye approximation that the surfaces were almost free[1] is not confirmed by the lattice-dynamical calculations.

The recoilless fraction of tin particles immersed in liquid paraffin has been measured by Suzdalev, Gen, Gol'danskii, and Makarov.[2] The smallest samples used by them were of diameter 250 Å. The corresponding cubes with the same number of atoms would have $N = 67$, which we found too large for numerical calculations because of the excessive computer time required. Experimentally f was found to be considerably smaller than f_∞, which suggests that the boundary conditions were of type (d), i.e., free surfaces and a softer binding of the surface atoms. It seems, however, that this model would not suffice for explaining the very large magnitude of the measured effect. At 93 °K, for example, $f_\infty = 0.350$, whereas for the 250-Å particles $f = 0.254$. Some additional mechanisms, like the softening of the force constants of a few surface layers, or a change in the lattice constant, might have been involved.

V. DISCUSSION

The recoilless fraction of microcrystals has been calculated from a lattice-dynamical model. The dependence of f on the boundary conditions has been found to follow the rule that f increases with increasing rigidness of the surfaces. This rule can be understood in terms of the following simple considerations. In a microcrystal with clamped surfaces, for example, the fixed surface atoms have a recoilless fraction $f = 1$. As the center of the crystallite is approached, the recoilless fractions of the individual atoms tend to f_∞. When averaged over all the atoms, f will thus turn out to be greater than f_∞. On the other hand, surface atoms of crystallites with free boundaries have large mean-square displacements and consequently their recoilless fraction will be smaller than f_∞. The average value of f will thus be smaller than f_∞.

The predictions of the modified Debye approximation for different boundary conditions do not follow the correct trend. It has been shown that the modified Debye approximation fails because it implicitly ignores the large changes which can occur in the mean-square displacements of the individual atoms of microcrystals and accounts only for changes which occur in the phonon frequency spectrum $N(\omega)$. The modified Debye approximation might still be useful for the explanation of physical effects in which $N(\omega)$ plays a main role, like the specific heat of microcrystals[4] or the enhanced transition temperature in small particles of superconductors.[32]

ACKNOWLEDGMENTS

The author wishes to thank Professor D. Schroeer and Professor W. A. Bowers for helpful discussions and for critical reading of the manuscript.

*Work supported by the Advanced Research Projects Agency through Contract No. SD-100 with the UNC Materials Research Center.

†On leave from the Soreq Nuclear Research Centre, Yavne, Israel.

[1]S. W. Marshall and R. M. Wilenzick, Phys. Rev. Letters 16, 219 (1966).

[2]I. P. Suzdalev, M. Ya. Gen, V. I. Gol'danskii, and E. F. Makarov, Zh. Eksperim. i Teor. Fiz. 51, 118 (1966) [Soviet Phys. JETP 24, 79 (1967)].

[3]S. Roth and E. M. Hörl, Phys. Letters 25A, 299 (1967); Acta Phys. Austriaca 27, 264 (1968).

[4]R. C. Thiel, Z. Physik 200, 227 (1967).

[5]F. R. L. Schoening, Acta Cryst. A24, 615 (1968).

[6]D. Schroeer, *Mössbauer Effect Methodology* (Plenum, New York, 1969), Vol. 5, p. 141.

[7]A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1966), Vol. 19, p. 1.

[8]E. R. Jones, J. T. McKinney, and M. B. Webb, Phys. Rev. 151, 476 (1966).

[9]R. M. Goodman, H. H. Farrell, and G. A. Somorjai, J. Chem. Phys. 48, 1046 (1968).

[10]J. M. Morabito, Jr., R. F. Steiger, and G. A. Somorjai, Phys. Rev. 179, 638 (1969).

[11]R. F. Wallis, B. C. Clark, and R. Herman, Phys. Rev. 167, 652 (1968).

[12]R. F. Wallis, B. C. Clark, R. Herman, and D. C. Gazis, Phys. Rev. 180, 716 (1969).

[13]A. Corciovei, D. Grecu, and E. Radescu, Z. Physik 209, 134 (1968).

[14]J. S. Van Wieringen, Phys. Letters 26A, 370 (1968).

[15]L. S. Kothari and C. M. Singal, Phys. Rev. 168, 952 (1968).

[16]E. W. Montroll and R. B. Potts, Phys. Rev. 100, 525 (1955); 102, 72 (1956).

[17]A. A. Mardudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic, New York, 1963).

[18]K. Patnaik and J. Mahanty, Phys. Rev. 155, 987 (1967).

[19]W. M. Visscher, Phys. Rev. 129, 28 (1963).

[20]M. Rich, Phys. Letters 4, 153 (1963).

[21]T. E. Feuchtwang, Phys. Rev. 155, 715 (1967).

[22]R. E. Allen and F. W. De Wette, Phys. Rev. 179, 873 (1969).

[23]A. A. Maradudin, Rept. Progr. Phys. 28, 331

(1965).
[24]D. C. Gazis, R. A. Toupin, and R. F. Wallis, Bull. Am. Phys. Soc. 8, 193 (1963).
[25]R. F. Wallis and D. C. Gazis, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon, New York, 1965), p. 537.
[26]A. A. Maradudin and J. Melngailis, Phys. Rev. 133, A1188 (1964).
[27]D. Schroeer, Phys. Letters 21, 123 (1966).
[28]D. J. Erickson, L. D. Roberts, T. O. Thomson, and J. W. Burton, Bull. Am. Phys. Soc. 15, 180 (1970).
[29]F. G. Karioris, J. J. Woyci, and R. R. Buckrey, in *Advances in X-Ray Analysis*, edited by J. B. Newkirk and G. R. Mallett (Plenum, New York, 1967), Vol. 10, p. 250.
[30]M. H. Rice, R. G. McQueen, and J. M. Walsh, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 6, p. 1.
[31]S. W. Marshall, Ph. D. thesis, Tulane University, 1965 (unpublished).
[32]A. Rothwarf, Phys. Letters 30A, 55 (1969).

PHYSICAL REVIEW B VOLUME 2, NUMBER 5 1 SEPTEMBER 1970

Electron-Nuclear Double Resonance of Mn^{2+} in $KMgF_3$ and K_2MgF_4

A. H. M. Schrama and P. I. J. Wouters
Natuurkundig Laboratorium der Universiteit van Amsterdam, The Netherlands*
and
H. W. de Wijn†
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
(Received 23 December 1969)

The ENDOR spectra of $^{55}Mn^{2+}$ in $KMgF_3$ and K_2MgF_4 have been measured at 4.2 °K. Whereas the spectrum in $KMgF_3$ could be analyzed in terms of a spin Hamiltonian of cubic symmetry, the spectrum in K_2MgF_4 shows axial anisotropy and appropriate axial terms had to be added. The principal results are for $KMgF_3$, $A/hc = (-91.347 \pm 0.007) \times 10^{-4}$ cm^{-1}; and, for K_2MgF_4, $D/hc = (+108 \pm 5) \times 10^{-4}$ cm^{-1}, $A/hc = (-90.809 \pm 0.018) \times 10^{-4}$ cm^{-1}, $B/hc = (-90.676 \pm 0.014) \times 10^{-4}$ cm^{-1}, and $Q'/h = 3e^2qQ/40h = (+0.19 \pm 0.04)$ MHz. A comparison with other compounds indicates that the anisotropic part of the hyperfine structure mainly results from a second-order process, linear in the axial component of the crystalline field and linear in the dipolar hyperfine coupling. Finally, the importance of the D term for the anisotropy field in antiferromagnetic K_2MnF_4 is pointed out.

I. EXPERIMENTAL RESULTS

In this paper we report electron-nuclear double resonance (ENDOR) measurements of the $^{55}Mn^{2+}$ ($S=\frac{5}{2}$, $I=\frac{5}{2}$) d^5 ^6S-state ion in $KMgF_3$ and K_2MgF_4. $KMgF_3$ has the cubic perovskite structure,[1] and the paramagnetic impurity Mn replaces Mg, which is at a site of cubic point symmetry with a sixfold coordination of nearest-neighbor F ions. K_2MgF_4 is a layer compound with tetragonal unit cell closely related to the perovskite structure.[2] Again Mn is in a sixfold coordination of F ions, but the cubic arrangement is slightly distorted along the crystalline c axis. The electron-spin resonance spectra (ESR) of these compounds have been studied previously.[3,4]

The data were taken at a temperature of 4.2 °K and a microwave frequency of 8.95 GHz with the experimental setup described previously.[5,6] The microwave power was increased to saturate the ESR spectrum to about half of the unsaturated intensity ($\gamma^2 H_1^2 T_1 T_2 \approx 1$). The Mn content of the crystals was between 0.1 and 1%. Roughly speaking, the ENDOR spectra each consists of six groups of five lines centered at the approximate frequencies of 95, 175, 380, 440, 670, and 690 MHz. Because of inhomogeneous broadening of the ESR lines, the ENDOR transitions were observable over several hundred gauss. The ENDOR frequencies were found to vary by a few percent in going from 2900 to 3400 G. The detailed analysis of the spectra has been done by means of diagonalization of the spin-Hamiltonian matrix, including all off-diagonal elements, followed by least-squares adjustment of the spin-Hamiltonian parameters to the measured line frequencies, as described before.[6] It appears that the six groups of lines are to be assigned to $m_S = -\frac{1}{2}, +\frac{1}{2}, -\frac{3}{2}, +\frac{3}{2}, -\frac{5}{2}$, and $+\frac{5}{2}$, respectively.

The ENDOR lines of Mn:$KMgF_3$ have been fitted