Influence of Force-Constant Changes and Localized Modes on the V:Fe^{57} Mössbauer System*

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An experimental and theoretical study is made of the Mössbauer effect of Fe^{57} in a vanadium matrix. We have measured the recoil-free fraction and second-order Doppler shift over the temperature range 100 to 700°K. The experimental results are interpreted using recently derived expressions for the mean-square velocity and displacement of the defect which allow for changes in the force constants as well as the mass at the impurity site. A good fit to the data is obtained for an increase in force constant of approximately 2.5. The data are also analyzed in the high-temperature limit to confirm this increase. Evidence for the presence of localized modes is found from the velocity shift, and the positions of the modes are determined.

1. INTRODUCTION

THE probability for the Mössbauer effect, its temperature dependence, and the temperature dependence of the second-order Doppler shift of the Mössbauer line are directly related to the dynamics of the Mössbauer-active nucleus.[1] When this nucleus is an impurity placed in a crystal, the lattice dynamics of the composite system influences the determination of the recoil-free fraction and the second-order Doppler shift. However, since an impurity has been introduced into the crystal, the dynamics is no longer that of the pure crystal. In particular there is a change in mass at the defect site and changes in force constants in the vicinity of this site. This perturbation can affect the mean-square displacement $\langle x^2\rangle$ and the mean-square velocity $\langle v^2\rangle$ of the impurity atom.

The evaluation of these quantities has been achieved for the case of an isotopic impurity.[1] Ignoring the change in force, the temperature dependence of the recoil-free fraction of Sn^{119} in V has been satisfactorily fitted.[2] For such calculations the essential input data is the density of states of the pure crystal, which is usually known experimentally. The influence of force-constant changes has not been taken into account quantitatively, except in the somewhat unphysical model of a simple cubic lattice with nearest-neighbor interactions only.[3] Recently[4] closed expressions for $\langle x^2\rangle$ and $\langle v^2\rangle$ have been derived for the central force body- and face-centered cubic crystal models in which there are changes in the nearest-neighbor forces around the defect site. Again the only required input data is the pure-crystal phonon spectrum.

Using these expressions it is then possible to fit the experimental data treating the force-constant ratio λ'/λ as a free parameter to be determined. As well as detailed fitting of the data at all temperatures, it is possible to obtain information from macroscopic fitting at the high-temperature limit. This is valuable since it serves as an indication to the force changes, and is also model-independent.

We have studied the system of Fe^{57} in V both experimentally and theoretically. In Sec. 2 we describe the theoretical situation at the microscopic and macroscopic levels. In Sec. 3 we describe the experimental determination of the recoil-free fraction and second-order Doppler shift and analyze the results in Sec. 4, where we find definite evidence for a big force-constant increase, and for the presence of localized modes. In Sec. 5 we discuss the sensitivity of the calculation to the various input parameters.

2. THEORETICAL ANALYSIS

The probability (f) of recoil-free γ-ray emission is given by

$$f=|\langle i|\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})|i\rangle|^2, \tag{1}$$

where $|i\rangle$ represents the initial and hence final state of the lattice. Here $\mathbf{r}$ is the position of the emitting nucleus and $\boldsymbol{\kappa}$ is the wave vector of the γ ray. Lipkin[5] has shown that under certain conditions, which we discuss later, we may write

$$f=\exp(-\kappa^2\langle x^2\rangle). \tag{2}$$

$\langle x^2\rangle$ is the mean-square displacement of the nucleus

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[1] A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18, p. 273. This review paper contains references to many related works in Mössbauer Spectroscopy and impurity problems.

[2] V. A. Bryukhanov, N. N. Delyagin, and Y. Kagan, Zh. Eksperim. i Teor. Fiz. 45, 1372 (1963) [English transl.: Soviet Phys.—JETP 18, 945 (1964)].

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

[4] P. D. Mannheim, this issue, Phys. Rev. 165, 1011 (1968).

[5] H. J. Lipkin, Ann. Phys. (N. Y.) 26, 115 (1964).

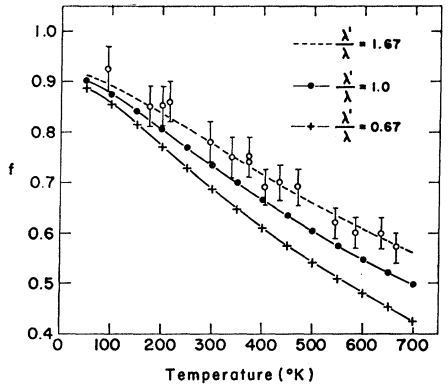

FIG. 1. The recoil-free fraction f as a function of temperature. The open circles represent the experimental points. The drawn lines are theoretical predictions for various force-constant changes.

vibrating in the lattice, and hence its determination is sufficient to calculate f.

The Mössbauer peak is also velocity-shifted due to the relativistic decrease in the mass of the nucleus as it emits the γ ray. We thus study the velocity shift, or second-order Doppler (SOD) shift

$$\Delta S=1/(2c)\langle v^2\rangle, \tag{3}$$

where $\langle v^2\rangle$ is the mean-square velocity of the nucleus. This is not in fact the measured shift, since we have to add to this the isomeric or chemical shift.

The system in which we are interested is an impurity in the bcc vanadium lattice. We consider changes in forces between the defect and its 8 nearest-neighbor host atoms in the harmonic approximation. Using group-theoretical techniques, which exploit the high (O_h) symmetry at the defect site, expressions for $\langle x^2\rangle$ and $\langle v^2\rangle$ have been obtained elsewhere for central forces only.[4] These expressions are in fact more general and also apply to a fcc lattice. We present here only the results.

For convenience we define

$$\rho(\omega)=\frac{M}{M'}-1+\frac{2\omega^2}{\omega_{\max}{}^2}\left(1-\frac{A_{xx}{}^{00}}{A'_{xx}{}^{00}}\right), \tag{4}$$

$$S(\omega)=\mathcal{P}\int\frac{\omega'^2\nu(\omega'^2)}{\omega'^2-\omega^2}d\omega'^2, \tag{5}$$

and

$$T(\omega)=\omega^4\int\frac{\nu(\omega'^2)}{(\omega^2-\omega'^2)^2}d\omega'^2. \tag{6}$$

Here $\nu(\omega^2)$ is the density of pure-crystal states in ω^2. M and M' are the masses of a pure-crystal atom and the impurity atom, respectively. $A_{xx}{}^{00}$ is the pure-crystal force constant, and $A'_{xx}{}^{00}$ is the modified force constant at the impurity site. The unknown $A_{xx}{}^{00}$ is replaced by $\omega_{\max}$, the experimentally known maximum frequency of the pure lattice, through the relation[4,6]

$$\omega_{\max}{}^2=\tfrac{1}{2}A_{xx}{}^{00}/M. \tag{7}$$

Then, as is shown in Ref. 4, localized (or resonance) modes are obtained if

$$1+\rho(\omega)S(\omega)=0. \tag{8}$$

The derived expressions for $\langle x^2\rangle$ and $\langle v^2\rangle$ are

$$\langle x^2\rangle=\frac{\hbar}{2M}\left(\frac{M}{M'}\right)^2\times\int_0^{\omega_{\max}}\frac{\coth(\frac{1}{2}\hbar\beta\omega)\nu(\omega)d\omega}{\omega\{[1+\rho(\omega)S(\omega)]^2+\frac{1}{4}\pi^2\omega^2\nu^2(\omega)\rho^2(\omega)\}}+\frac{\hbar}{2M}\left(\frac{M}{M'}\right)^2\frac{\coth(\frac{1}{2}\hbar\beta\omega_L)}{\omega_L}\times\left[\rho^2(\omega_L)T(\omega_L)+\frac{M}{M'}-[1+\rho(\omega_L)]^2\right]^{-1}, \tag{9}$$

$$\langle v_x{}^2\rangle=\frac{\hbar}{2M}\left(\frac{M}{M'}\right)^2\times\int_0^{\omega_{\max}}\frac{\omega\coth(\frac{1}{2}\hbar\beta\omega)\nu(\omega)d\omega}{\{[1+\rho(\omega)S(\omega)]^2+\frac{1}{4}\pi^2\omega^2\nu^2(\omega)\rho^2(\omega)\}}+\frac{\hbar}{2M}\left(\frac{M}{M'}\right)^2\omega_L\coth(\frac{1}{2}\hbar\beta\omega_L)\times\left[\rho^2(\omega_L)T(\omega_L)+\frac{M}{M'}-[1+\rho(\omega_L)]^2\right]^{-1}, \tag{10}$$

where $\beta=1/KT$, and the second term in each expression only contributes if there is a localized mode with frequency ω_L. Though only the force constant at the defect site appears in the final expressions, force constants connecting the defect to the neighbors have in fact been included, since in a central force model they are related to $A_{xx}{}^{00}$, and can hence be eliminated. The equations thus contain one extra parameter, the force-constant ratio, which we shall write as λ/λ'. When we set $\lambda/\lambda'=1$, we regain the standard expressions for an isotopic impurity.[1] As is seen from (8), (9), and (10), for calculative purposes we need only know $\nu(\omega)$. These expressions are temperature-dependent through the population factor. However, at high temperatures we are near the classical limit and hence we can obtain simpler forms for comparison with the experimental data.

In the classical limit momentum and position commute. This means that $\langle x^2\rangle$ is only affected by the changes in the potential energy, and is independent of

[6] P. D. Mannheim, M.Sc. thesis, Weizmann Institute of Science, Rehovoth, 1966 (unpublished).

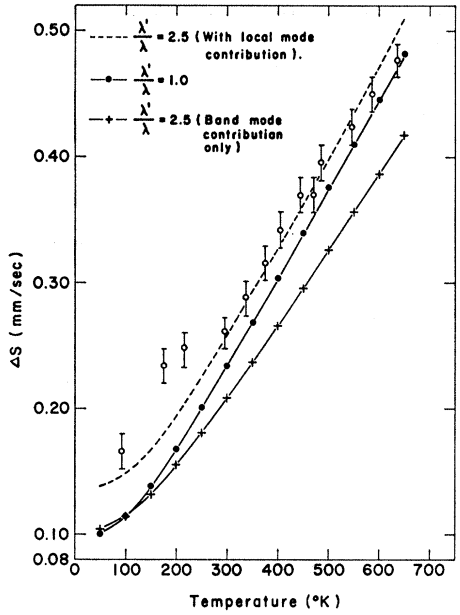

FIG. 2. The second-order Doppler shift ΔS as a function of temperature. The drawn lines show the effect of the force-constant change and of the localized modes.

any change in mass, which would only appear in the kinetic energy. This behavior is exhibited in the formula of Maradudin,[7]

$$\langle x^2\rangle_{\mathrm{Cl}}=\frac{KT}{M}\mu_{-2}+\frac{KT}{M^2}\frac{1}{\mu_2{}^2}(A_{xx}{}^{00}-A'_{xx}{}^{00})+\cdots$$
$$=\frac{KT}{M}\mu_{-2}+\frac{KT}{M}\frac{\omega_{\max}{}^2}{2\mu_2{}^2}\left(1-\frac{\lambda'}{\lambda}\right)+\cdots, \qquad (11)$$

using Eq. (7). Here μ_2 and μ_{-2} are moments of the frequency distribution

$$\mu_n=\int\omega^n\nu(\omega)d\omega. \qquad (12)$$

The above formula was derived using an expansion in powers of $1-\lambda'/\lambda$ and is only valid if $\lambda'/\lambda\sim 1$. Thus, if $\langle x^2\rangle_{\mathrm{Cl}}$ differs only by a small amount from the first term of (11) [$\langle x^2\rangle_{\mathrm{Cl}}$ being determined from the experimental f], we can estimate λ'/λ. It is evident from (11) that at high temperatures the recoil-free fraction is strongly sensitive to changes in force, and provides at least a clear indication of the sign of the change. Further, we can expect that at low temperatures, where quantum corrections become important, f will become less sensitive to λ'/λ as terms dependent on the change in mass are also introduced.

It is also possible to treat quantitatively the other extreme case, namely $\lambda'/\lambda\gg 1$, at high temperatures. Here the motion of the defect will be strongly localized and it will have the frequency[6]

$$\omega_{\mathrm{cell}}{}^2=A'_{xx}{}^{00}/M' \qquad (13)$$

as if it moves in an harmonic cell potential provided by the static lattice, with $\omega_{\mathrm{cell}}\gg\omega_{\max}$. Then from the equipartition of energy we have

$$\langle x^2\rangle=KT/A'_{xx}{}^{00}=KT/M'\omega_{\mathrm{cell}}{}^2. \qquad (14)$$

As is seen from (14), the recoil-free fraction is close to unity at ordinary temperatures in the case of a strongly localized mode. Therefore we expect that it will display a slow variation in temperature at lower temperatures.

From the commutation argument we can also study the high-temperature behavior of $\langle v^2\rangle$. In the pure classical limit $\langle v^2\rangle$ is independent of the force change and only depends on the defect mass. The first quantum correction introduces λ'/λ, so that, as shown by Maradudin,[8] the velocity shift ΔS is given by

$$\Delta S=\frac{\langle v^2\rangle}{2c}=\frac{3KT}{2M'c}\left\{1+\frac{1}{12}\left(\frac{\hbar}{KT}\right)^2\frac{A'_{xx}{}^{00}}{M'}+\cdots\right\}$$
$$=\frac{3KT}{2M'c}\left\{1+\frac{1}{12}\left(\frac{\hbar}{KT}\right)^2\frac{M}{M'}\frac{\frac{1}{2}\omega_{\max}{}^2}{\lambda}\right\}. \qquad (15)$$

This formula is obtained from an expansion in powers of $\hbar$ and is valid for any λ'/λ. The first term is the pure classical limit. We see that at high temperatures we can estimate λ'/λ from the experimental SOD shift. This is not very accurate though, since the SOD shift differs only slightly from the pure classical limit. However at lower temperatures quantum corrections become important, so that here we can hope to distinguish between force-constant ratios.

These considerations will become evident in Sec. 4 where expressions (9) and (10) are used in the calculation. [See, e.g., Figs. (1) and (2).]

3. EXPERIMENTAL

Experiments were done with the 14.4-keV line of Fe^{57} embedded in vanadium. Sources of Co^{57}, the parent nucleus of Fe^{57}, diffused in vanadium, were prepared for this reason. The concentration of the Co^{57} (Fe^{57}) impurities in these samples is estimated to be $\sim 1:10^6$ in atoms. A linear velocity Mössbauer system[9] was used where the source was moving with respect to a stationary $Na_4Fe(CN)_6\cdot 10H_2O$ (0.25 mg/cm^2 in Fe^{57}) absorber. Mössbauer spectra were taken in the temperature range 90 to 700°K. A small oven attached to the driving rod was used for the variation of the temperature. A liquid-nitrogen cryostat, similar to that described by

[7] A. A. Maradudin and P. A. Flinn, Phys. Rev. 126, 2059 (1962).

[8] A. A. Maradudin, P. A. Flinn, and S. L. Ruby, Phys. Rev. 126, 9 (1962).

[9] H. Brofman, M. Greenshpan, and R. H. Herber, Nucl. Instr. Methods 42, 245 (1966).

Pasternak *et al.*[10] was used for lower than room temperatures. The absorber was kept at room temperature in all measurements.

4. RESULTS

The recoil-free fraction was calculated from the area under the absorption peak. By comparing the absorption area A of the vanadium spectrum to that displayed by a standard Cu source, we can find the recoil-free fraction of the former by the relation

$$f_V = f_{Cu}(A_V)/A_{Cu}. \tag{16}$$

The recoil-free fraction of Fe^{57} in Cu has been measured by several investigators[11,12] and the Cu (Fe^{57}) system is often used as a standard source. The results calculated from (16) were corrected for background. The total error in the so determined absolute values of the recoil-free fraction was 5% or less.

The total shift ϵ of the Mössbauer line is given by

$$\epsilon = \delta + \Delta S_s - \Delta S_a, \tag{17}$$

where δ is the chemical shift of Fe^{57} in vanadium with respect to the sodium ferrocyanide absorber, and ΔS_s and ΔS_a are the SOD shifts of the source and absorber respectively. In order to determine the shift of the source, it is necessary to separate the part $(\delta - \Delta S_a)$ from the total shift ϵ. This can be done in the high-temperature range where Eq. (15) holds and the chemical shift is temperature-independent.[11] Combining (15) and (17) we have

$$\epsilon - \frac{3KT}{2M'c} = (\delta - \Delta S_a) + \left(\frac{1}{16}\frac{\hbar^2}{K}\frac{M}{M'}\frac{\omega_{max}^2}{M'c}\frac{\lambda'}{\lambda}\right)\frac{1}{T}. \tag{18}$$

Least-square fitting of the parameters of Eq. (18) to the experimental results for the temperature range 300 to 700°K gives

$$\delta - \Delta S_a = -0.153 \pm 0.007 \text{ mm/sec}.$$

In Fig. 1 we have plotted the recoil-free fraction and in Fig. 2 the velocity shift, both as functions of temperature. For the recoil-free fraction we have also plotted the calculated f using formula (9) for three values of λ'/λ. For the calculation we have used the experimental density of states of Eisenhauer *et al.*,[13] taking the cutoff at $\omega_{max} = 6.3 \times 10^{13}$ secs^{-1}. When $\lambda'/\lambda = 1.0$, the case of change in mass only, the measured f is consistently underestimated at all temperatures. A weakening of the forces $\lambda'/\lambda = 0.67$ is seen to reduce f even more. The best fit to the data is obtained with $\lambda'/\lambda = 1.67$. Good fits will also be obtained for slightly stronger or weaker forces in the range 1.5–2.25, with f increasing with λ'/λ. The case of $\lambda'/\lambda = 2.25$ is interesting. With this force-ratio condition (8) yields a localized mode just outside the band. We have fitted the data using $\lambda'/\lambda = 2.25$, reckoning only the band modes. The localized-mode contribution to the Debye-Waller factor is certainly small, i.e., about 2% because of the factor $1/\omega$ in (9). Also the population factor is small. However, at nonzero temperatures the system is not in a pure state prior to γ emission, so a density matrix has to be introduced. As is shown in Refs. (1) and (5) this correction reduces to a Bessel-function factor which only takes appreciable contributions from localized modes. Thus for $\lambda'/\lambda < 2.25$ we had no need to consider it at all in calculating f. Maradudin[1] suggests that the effect of this Bessel function is to counteract the contribution of the localized mode to $\langle x^2 \rangle$. Lipkin,[5] however, points out that this term will not be relevant if the lattice relaxes in a shorter time than the nuclear level lieftime. Estimates of the lifetime of localized modes due to anharmonicity suggest that this is in fact the case. Thus, in the case that the localized mode is short-lived, the experimental fit is only in the range $1.5 < \lambda'/\lambda < 2.0$. We can also examine the macroscopic fit to the recoil-free fraction. From the density of states we find $\mu_{-2} = 4.45/\omega_{max}^2$. At 600° the leading term in (11), which neglects the force change, then gives $f = 0.55$. Experimentally $f = 0.6$, which indicates a definite increase in force. This increase is too large to allow a fitting of the correction term in (11).

In Fig. (2) the experimental values of the velocity shift and its values calculated from formula (10) for $\lambda'/\lambda = 1$ and $\lambda'/\lambda = 2.5$ are plotted. Again it is seen that in the absence of an increase in force the SOD shift is underestimated. The best fit is with $\lambda'/\lambda = 2.5$. Here there is a localized mode about 2% outside the band as calculated from Eq. (8) and its contribution to $\langle v^2 \rangle$ is appreciable. This is to be expected since the contribution goes as ω. To emphasize this we have plotted the calculated values both with and without including the localized mode. We find that we can fit the data for λ'/λ in the range 2.5 to 10, and that it is impossible to fit ΔS for any force-constant ratio without a localized-mode contribution. A broad fit to $\langle v^2 \rangle$ is expected since, as argued in Sec. 2, at higher temperatures the force-constant effect is small. In the range 1.5 to 2.25 we cannot in fact fit the data because localized modes, which are necessary to raise the value up, are not quite produced. However, this is strongly dependent on the cutoff position. Taking $\omega_{max} = 6.0 \times 10^{13}$ sec^{-1}, we then have localized modes in this range with which a fit can be achieved.

The low-temperature fitting is a little unsatisfactory. However, this may be an indication that the chemical shift is in fact temperature-dependent in this region. We determined the velocity shift assuming the constant chemical shift determined at high temperatures. The experiments of Steyart and Taylor,[11] as well as the

[10] M. Pasternak, A. Simopoulos, and Y. Hazoni, Phys. Rev. **140**, 1892 (1965).
[11] W. A. Steyart and R. D. Taylor, Phys. Rev. **134**, A716 (1964).
[12] R. M. Housley, J. G. Dash, and R. H. Nussbaum, Phys. Rev. **136**, 464 (1964).
[13] C. M. Eisenhauer, I. Pelah, D. J. Hughes, and H. Palevsky, Phys. Rev. **109**, 1046 (1958).

present work, indicate that the chemical shift is constant at high temperatures. However there is no evidence for constancy at low temperatures also.

One may make an estimate of the force change from the high-temperature limit. At 600° the leading term of (15) is 0.447 to be compared with an experimental 0.462. This again indicates an increase in force, in the range $1.5<\lambda'/\lambda<4$, allowing for the errors in the measured values.

The detailed calculations of $\langle x^2\rangle$ and $\langle v^2\rangle$ were done numerically on the Golem computer at the Weizmann Institute of Science.

5. DISCUSSION

It is interesting to study the variation of our results with changes in ω_{max} and $\nu(\omega)$. For comparison we also calculated f and the SOD shift using the density of states of Gläser *et al.*[14] Taking first the cutoff at 6.3×10^{13} secs^{-1} we fit f for values of λ'/λ in the range 3–10, with a best fit at $\lambda'/\lambda=5$. Fitting to the SOD shift is achieved in the same range with a best fit again at $\lambda'/\lambda=5$. Localized modes begin to appear in this case at $\lambda'/\lambda=1.8$, so for $\lambda'/\lambda=5$ there is a localized mode at $1.1\omega_{max}$. This mode makes the main contribution to the SOD shift as may be seen from (10).

With the same density of states and the higher cutoff, 7.6×10^{13} sec^{-1}, indicated by Gläser *et al.*, it is impossible to fit the data at all, even with infinite λ'/λ. This comparison is valuable since it helps understanding whether the high-energy tail observed by Gläser *et al.* and Chernoplekov *et al.*[15] is due to one-phonon or many-phonon effects. On general grounds Van Hove[16] has shown that the high-energy behavior of the density of states should show a sharp drop after the longitudinal mode maximum with a sharp cutoff. Since we are doing a model calculation for the crystal anyway, it seemed reasonable to choose the Eisenhauer *et al.* density of states which satisfies best the Van Hove requirements. If we artificially cut off the tail in the spectrum of Gläser *et al.*, then again there is good agreement with experiment, though with a high force ratio. No cutoff higher in the tail will do, which suggests that the observed tail is not due to one-phonon effects.

There is very little now between choosing the data of Eisenhauer *et al.*, or of Gläser *et al.* without the tail. However the data of Gläser *et al.* require a very big increase in force, which seems unreasonable. Also, in the macroscopic fit, which is model-independent, the lower force ratio is favored.

There is also a strong sensitivity to ω_{max}. This occurs when there are changes in force because of the second term in $\rho(\omega)$ in Eq. (4), so that ω_{max} also appears in the integrand. When there is no change in force, the only dependence on ω_{max} would be in the range of integration.

One of the most interesting features of the results is the evidence from the SOD shifts for the presence of localized modes. It is usually thought that since $\langle v^2\rangle$ is an average over the whole spectrum, studies of localized modes by zero-phonon Mössbauer experiments are not possible and that measurements which scan the whole spectrum are necessary to observe localized modes directly. However, we can infer the presence of localized modes from the results and make a good estimate of the position of the modes.

The results confirm conclusively the importance of the change in force constants, contrary to a suggestion of Bryukhanov *et al.* that "the local substructure of the lattice seems to give a weakening of the effect of a change in the force constants."[2]

There are some limitations to the calculation. We neglect anharmonicity and defect interactions and assume substitutional occupancy of a lattice site. In the present experiments the concentration was 1 part in 10^6, so there should be no need to consider concentration effects. The main assumption of the work, however, is that there are only central forces. The impossibility of fitting the results with a definite value of λ'/λ perhaps suggests a strong noncentral component. The observed density of states of vanadium does not indicate this noncentral component, though there is in fact some discussion on the point.[13]

ACKNOWLEDGMENT

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[14] W. Gläser, F. Carvalho, and G. Ehret, in *Symposium on Inelastic Scattering of Neutrons, Bombay, 1964* (International Atomic Energy Agency, Vienna, 1965), Vol. I, p. 99.

[15] N. A. Chernoplekov, M. G. Zemlyanov, and A. G. Chicherin, Zh. Eksperim. i Teor. Fiz. **43**, 2080 (1962) [English transl.: Soviet Phys.—JETP **16**, 1472 (1963)].

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