Fine Structure in the Absorption Spectra of KMnF₃ and RbMnF₃

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Experimental studies of the absorption spectra in the 3900 Å region of KMnF₃ and RbMnF₃ at 4.2°K are presented. The spectra of the two substances are almost identical, and show the same number of lines and same type of fine structure. The $^4\Gamma_3$ levels, split by the tetragonal component of the crystalline field, are associated with observed transitions at ~3939 and ~3896 Å. Definite energy-level patterns are found for the weak vibrational lines accompanying these transitions. A sharp and very weak magnetic dipole line M is found (with three components) at ~3976 Å. An electric dipole line P_1 at ~3966 Å appears to be a magnon sideband of the magnetic dipole line. M is presumed to be an exciton line associated with the electric dipole transition P_2 at ~3955 Å to the main $^4\Gamma_1$ level. The electric dipole lines P_1 and P_2, associated with the $^4\Gamma_1$ level, show a fine structure which is interpreted in terms of exchange-coupled pairs of ions with a spin Hamiltonian $-2J\,S_1 \cdot S_2$. The selection rule for these transitions is that the total spin of the pair is conserved.

1. INTRODUCTION

AT 88.3[1] and 82.6°K[2] KMnF₃ and RbMnF₃ have the perovskite structure and become antiferromagnetic. The Rb compound has a simple-cubic magnetic structure with a very small anisotropy. Teaney et al.[2] find the exchange and anisotropy fields to be $H_E = 8.9 \times 10^5$ Oe and $H_A = 447$ Oe. Neutron-diffraction studies[3] suggest that the anisotropy field is less than 400 Oe, and that the exchange field (based on $J = 3.4°K$) is $H_E = 7.6 \times 10^5$ Oe. KMnF₃ has a more complicated magnetic behavior. It is a uniaxial antiferromagnet to about 70°K, and at lower temperatures goes into a canted structure with a weak ferromagnetism. Its exchange and anisotropy fields do not seem to be as well known as those of RbMnF₃. From Smart's[4] data, we estimate that $H_E = 6.9 \times 10^5$ Oe to 8.0×10^5 Oe, and from the experiments of Heeger et al.[1] $H_A = 2.9 \times 10^4$ Oe. The exchange and anisotropy fields will be of use in the interpretation of the spectra of these compounds.

The major features of the absorption spectra of these compounds are due to the $(MnF_6)^{4-}$ complex. The Mn²⁺ ion finds itself in an octahedral array of F⁻ ions, and the Mn-F separations appear to be about the same for both substances. Thus one would expect the spectra to be very similar, as is indeed the case.

In this paper we present results for the transitions from the $^6\Gamma_1$ ground state to the $^4\Gamma_1$, and lower $^4\Gamma_3$ excited states. (We use here the notation of Koster et al., and Jorgensen.[5]) The electron configuration in ground

and excited states is the same, $\gamma_5^3 \gamma_3^2$, and the transition energies are independent of the octahedral crystal field splitting energy. Crystal field theory says that the $^4\Gamma_1$ and $^4\Gamma_3$ levels are degenerate, but in fact they are separated slightly presumably because of covalency in the crystal.[6]

Previous studies of the spectrum of KMnF₃ have been made by Ferguson et al.,[7] and of both crystals by Stevenson.[8] In this paper some new data are presented which give information on the magnetic interactions in the crystals.

2. EXPERIMENTAL

The crystals used were in the form of flat plates approximately 1 cm on the side and 1 mm thick. They had a fairly good optical appearance, with the characteristic clear, pink colour of Mn²⁺ compounds.

The spectra were taken on a Bausch and Lomb model 11 grating spectrograph, using a variety of photographic emulsions; Kodak Spectrum Analysis 1 and 3, type 103 a-O and type 103-F. The type 103-F, although slightly grainy, has a very fortunate emulsion characteristic for this type of work, and allowed the observation of detail which could be seen only with great difficulty on the other emulsions.

Wavelengths were obtained from the spectrum of a mercury lamp, and are estimated to be accurate to within about ±0.15 Å (about ±1 cm⁻¹ in the energy). In some cases a line was seen on only one or two spectra, and the accuracy may be worse. Also some lines are very broad and an estimate of accuracy loses any meaning; in these cases the wavelength given is for what is judged to be the middle of the line.

Typical spectra at 4.2°K are shown in Fig. 1; the wavelengths given are the averages from all the spectra. It is impossible to observe all the detail with one exposure. The very weak lines are studied at short exposures, and the strong lines at longer exposures. The

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[7] J. Ferguson, H. J. Guggenheim, and Y. Tanabe, J. Appl. Phys. 36, 1048 (1965); Phys. Rev. Letters 14, 737 (1965).

[8] R. Stevenson, Can. J. Phys. 43, 1732 (1965).

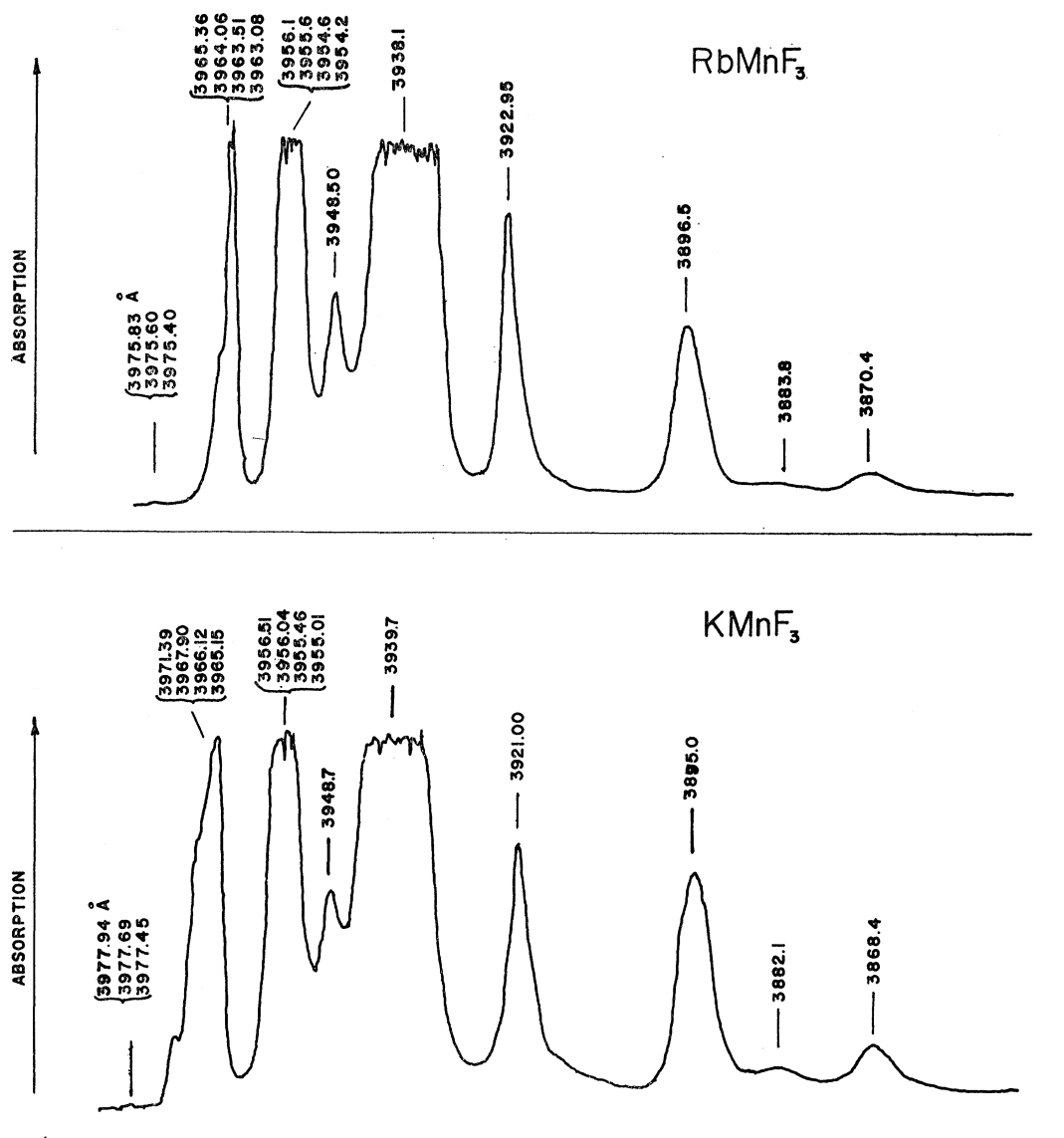FIG. 1. Absorption spectra of KMnF₃ and RbMnF₃ at 4.2°K. Wavelengths are in angstrom units. The vertical ordinate represents absorption in terms of decreasing plate density.

densitometer tracings reproduced in Fig. 1 were chosen as those which seemed to show the most detail, for display purposes, and also to show the remarkable similarity between the spectra of the two compounds. The vertical axis in this figure is decreasing film density. This has an approximately logarithmic characteristic so that Fig. 1 should not be used to judge line shapes or intensities. On the other hand the crystal thicknesses, exposures, etc. were the same for both crystals so that we can conclude from Fig. 1 that intensities of corresponding lines in the two crystals are approximately the same. The apparatus used here was not suitable for quantitative intensity determinations. The wavelengths of KMnF₃ agree well with those given by Ferguson

et al.[7] In Table I the observed spectral lines with their energies are shown. The assignment of the lines will be explained in the next section.

3. DISCUSSION

The spectra of these two substances have the same number of lines, and these lines have the approximately the same intensity relative to each other. The spectra are remarkably similar, but superficially are quite dissimilar to the spectra of MnF₂ and CsMnF₃. We will describe the details of the spectra of MnF₃ and CsMnF₃ in another paper, but it is convenient to quote some results here in order to facilitate the assignment of the observed lines.

TABLE I. Observed spectral lines at 4.2°K.

Assignment		KMnF$_3$ λ (Å)	KMnF$_3$ ϵ (cm^{-1})	RbMnF$_3$ λ (Å)	RbMnF$_3$ ϵ (cm^{-1})
	M	3977.94	25138.6	3975.83	25152.0
		3977.69	25140.2	3975.60	25153.4
		3977.45	25141.7	3975.40	25154.7
$^4\Gamma_1$	P_1	3971.39	25180.1	3965.36	25218.4
		3967.90	25202.2	3964.06	25226.7
		3966.12	25213.6	3963.51	25230.2
		3965.15	25219.7	3963.08	25232.9
	P_2	3956.51	25274.8	3956.1	25277.4
		3956.04	25277.8	3955.6	25280.6
		3955.46	25280.9	3954.6	25287.0
		3955.01	25284.4	3954.2	25289.6
	$A-\delta_1$	3948.7	25324.8	3948.50	25326.1
	A	3939.7	25382.6	3938.1	25393.0
$^4\Gamma_3$	$A+2\delta_1$	3921.00	25503.7	3922.95	25491.0
	B	3895.0	25673.9	3896.5	25664.1
	$B+\delta_2$	3882.1	25759.3	3883.8	25748.0
	$B+2\delta_2$	3868.4	25850.5	3870.4	25837.1

FIG. 2. Energy-level pattern for transitions to the $^4\Gamma_3$ state. The parameters measured by experiment are given in Table III.
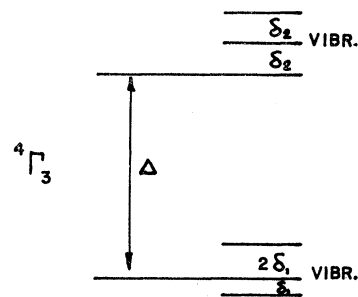
SINGLE-ION
TRANSITIONS

In this wavelength region the spectra of the four Mn^{2+} fluorides is not affected by the octahedral crystal field splitting, and since the (MnF$_6$)$^{4-}$ complex is almost identical from crystal to crystal one would expect that the spectra would also be identical in their major features. Dissimilarities should be minor and should be confined to the vibrational structure and to fine structure which arises from the magnetic interactions.

An inspection of the spectra shows that this basic similarity does indeed exist. The results are shown in Table II. Our assignment is that the line at $\sim$3955 Å corresponds to the transition $^6\Gamma_1 \rightarrow {}^4\Gamma_1$. The degeneracy between $^4\Gamma_1$ and $^4\Gamma_3$ is removed by covalency in the crystal. The lines at $\sim$3938 and $\sim$3890 Å correspond to transitions to the $^4\Gamma_3$ level which is split into components A and B by a tetragonal component of the crystal fields. In all cases a fine structure associated with the $^4\Gamma_1$ level is observed, whereas no fine structure is observed on the $^4\Gamma_3$ levels.

This assignment is similar to that of Stout[9] for MnF$_2$ but is different from that proposed by Ferguson et al.[7] for KMnF$_3$. Ferguson et al. assign the line at $\sim$3940 Å to the $^4\Gamma_1$ level, and lines at $\sim$3955 and $\sim$3967 Å to the tetragonally split $^4\Gamma_3$ level. We believe that their assignment is incorrect for reasons which will be described in the remainder of the paper.

TABLE II. Major line assignments for the Mn^{2+} fluorides.

	$^4\Gamma_1$ (Å)		$^4\Gamma_3A$ (Å)	$^4\Gamma_3B$ (Å)
KMnF$_3$	3955	(P)	3939.7	3895.0
RbMnF$_3$	3955	(P)	3938.1	3896.5
MnF$_2$ (σ)	3956	(P)	3929.6	3889.4
MnF$_2$ (π)	3956		3929.2	3888.4
CsMnF$_3$ (σ)	3956	(P)	3930.6	3890.1
CsMnF$_3$ (π)	3956		2928.9	3884.4

[9] J. W. Stout, J. Chem. Phys. 31, 709 (1959).

With the basic assignment of lines given in Table II it is found that the remainder of the spectral lines observed for these crystals can be interpreted in terms of characteristic energy level diagrams. The simplest diagram is for the transitions to the $^4\Gamma_3$ states, shown in Fig. 2. The main splitting Δ of the lines is thought to be due to the tetragonal component of the crystal field. The weak subsidiary lines spaced by characteristic energies δ_1 and δ_2 would then be vibrational in nature. These energy parameters are given in Table III. Because of their intensity these lines would seem to be single-ion electric dipole transitions which are vibrationally induced. The very intense $^4\Gamma_3A$ line was closely examined for a fine structure which might indicate exchange coupling of ion pairs, but no such fine structure was observed.

The remainder of the lines are associated with the $^4\Gamma_1$ level and form an interesting and complicated sequence of events. Our rendering of the experimental results is shown in the energy-level diagram Fig. 3. Let us first confine our attention to the two groups of 4 lines called P_1 and P_2 in Table I. These are interpreted by supposing that pairs of ions on adjacent sublattices are coupled by the indirect exchange interaction. The $^6\Gamma_1$ ground state has an interaction of magnitude J_0

TABLE III. Experimentally measured parameters of $^4\Gamma_3$ levels. (See Fig. 2)

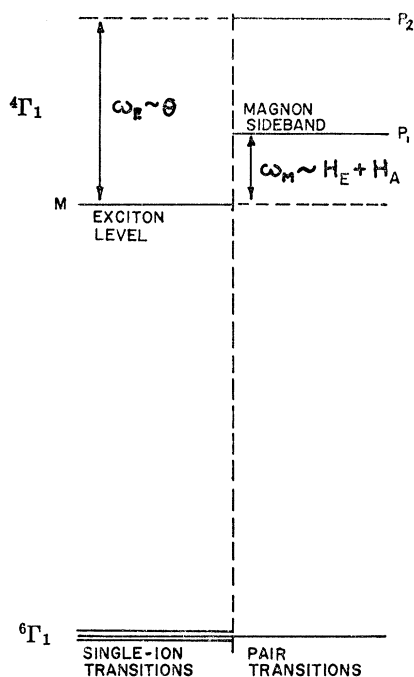|	Δ (cm^{-1})	δ_1 (cm^{-1})	δ_2 (cm^{-1})
RbMnF$_3$	271	55	86
KMnF$_3$	291	60	87

FIG. 3. Energy-level pattern for transitions to the $^4\Gamma_1$ state.

and splits into six levels corresponding to different total pair spin $S_p = 0, 1, \cdots, 5$. The excited states P_1 and P_2 have interactions J_1 and J_2 and split into 4 levels each. In the ground state both ions have spin $S = \frac{5}{2}$, whereas in the excited states both ions have spin $\frac{3}{2}$. The spin Hamiltonian is $-2J\mathbf{S}_1 \cdot \mathbf{S}_2$ and transitions are observed with the selection rules $\Delta S_p = 0$. This type of fine structure was first observed for Mn^{2+} ions by McClure,[10] and was observed in Mn^{2+}: $KZnF_3$ by Ferguson et al.[7] In the present results the fine structure fits this interpretation accurately for P_1 and P_2 in $KMnF_3$ and for P_1 in $RbMnF_3$. The fine structure on P_2 in $RbMnF_3$ does not fit this pattern, but this is thought to be due to the uncertainty of the measurement. The exchange coupling constants for the excited states evaluated in this way are given in Table IV. It is interesting to note that $KMnF_3$ appears to show a ferromagnetic interaction in P_1.

The work of Ferguson et al.[7] has shown that P_1 and P_2 are electric dipole transitions, and also that P_1 and P_2 merge together at about 70°K. They suggest that the separation of P_1 and P_2 below 70°K is due to a tetragonal distortion, but the detail of the present spectra suggest that another interpretation may be

TABLE IV. Exchange-interaction parameters of $^4\Gamma_1$ states.

	J_0 (cm^{-1})	J_1 (cm^{-1})	J_2
$RbMnF_3$	-2.4[3]	-1.2	$\cdots$
$KMnF_3$	-2.2[4]	$+1.0$	-2.9

[10] D. S. McClure, J. Chem. Phys. **39**, 2850 (1963).

preferable. There is a very weak and very sharp triplet, which we call M, at ~ 3977 Å. The weakness and sharpness of this line indicates that it is a magnetic dipole transition. (We will speculate later on the meaning of its three components). Line M is separated in energy from P_1 by a quantity which appears to be equal to $\omega_M \sim (H_E + H_A)$ the maximum magnon energy at the Brillouin-zone boundary. The experimentally measured energy quantities, indicated on Fig. 3, are given in Table V. The calculated values of ω_M are; for $RbMnF_3$ using $H_E = 7.6 \times 10^5$ Oe,[3] $H_A = 0$, $\omega_M = 71$ cm^{-1}, and for $KMnF_3$ using $H_E = 6.9 \times 10^5$ Oe,[4] $H_A = 2.9 \times 10^4$ Oe,[1] $\omega_M = 68$ cm^{-1}. The arrangement of levels is very reminiscent of the magnon sidebands in MnF_2 found by Greene et al.[11] and studied in a number of papers.

The present results can be tentatively interpreted by supposing that line P_1 is a magnon sideband of the magnetic dipole line M. Line M is presumably an exciton line associated with P_2, the $^4\Gamma_1$ level. Then according to this interpretation the incoming photon interacts with the Mn^{2+} ion in such a way that an exciton is emitted along with a high-energy magnon. The sharpness of the "exciton" line M brings to mind the Mössbauer analogy described by Silsbee and Fitchen.[12]

TABLE V. Experimentally measured parameters of $^4\Gamma_1$ levels. (See Fig. 3)

	ω_E (cm^{-1})	ω_M (cm^{-1})	Zero-splitting-field (cm^{-1})
$RbMnF_3$	131	75	1.4
$KMnF_3$	139	67	1.5

Its splitting into three components may be associated with an enhanced zero-field splitting of the $^6\Gamma_1$ ground state. Paramagnetic-resonance experiments[13] indicate that the ground state of the Mn^{2-} ion is split into 3 Kramers doublets separated by about 0.1 cm^{-1}. Should the 3 components of M be associated with a zero-field splitting of the $^6\Gamma_1$ level, then some mechanism has caused an enhancement of the splitting by more than an order of magnitude. *Note added in proof.* Such a splitting of the ground state may be a result of zero-point spin deviations; see A Misetich and R. E. Dietz, Phys. Rev. Letters **17**, 392 (1966). One last correlation between measured energy quantities and those known in other ways can be noted. The separation between M and P_2, which we have called ω_E in Fig. 3 and Table V, is approximately equal to the energy associated with the Curie-Weiss constant θ; this correlation may, of course, be quite accidental.

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[13] B. Bleaney and D. J. E. Ingram, Proc. Roy. Soc. (London) **A205**, 336 (1951); I. Hayushi and K. Ono, J. Phys. Soc. Japan **8**, 270 (1953).

4. SUMMARY

The main conclusions of the present research can be summarized as follows:

(a) Vibrationally induced electric-dipole lines associated with the transition to the tetragonally split $^4\Gamma_3$ level are observed at $\sim$3939 and $\sim$3896 Å.

(b) Fine structure associated with exchange-coupled pairs of ions is observed on electric dipole transitions associated with the $^4\Gamma_1$ level. The fine structure involves pairs of ions in a $S=\frac{5}{2}$ ground state, both being excited into a $S=\frac{3}{2}$ upper state. The selection rule for the transitions is that the spin of the pairs is conserved.

(c) The fine structure due to exchange coupled pairs of ions seems to be associated only with the $^4\Gamma_1$ levels.

(d) The $^4\Gamma_1$ level is not vibrationally induced. Some other mechanism is operative, which is tentatively associated with the excitation of an exciton causing a sharp magnetic dipole line and the consequent excitation of a magnon which causes an electric-dipole satellite line.

Experimental Study of the Lattice Dynamics of Disordered Vanadium Alloys*

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We report on the investigation of the vibrational frequency spectrum of disordered alloys of vanadium consisting of $Be_{0.033}V_{0.967}$ $Ni_{0.05}V_{0.95}$, and $Pt_{0.05}V_{0.95}$. Inelastic-neutron-scattering techniques were used to obtain information about the frequency spectrum of these alloys. The alloys were chosen because they scatter neutrons incoherently, and yet the solute atoms can differ widely from vanadium with respect to atomic mass and electron configuration. The disordered vibrational spectra show high-frequency impurity bands upon alloying with light-mass beryllium impurity atoms, large changes in the whole vibrational pattern caused by long-range interatomic potential differences arising from changes in the electronic properties of the nickel and platinum alloys, and most surprisingly, very small changes in the vibrational spectra upon alloying with heavy-mass platinum impurities.

INTRODUCTION

IN a communication published several years ago, we reported inelastic-neutron-scattering measurements of localized modes of vibration associated with light-mass nickel atoms in nickel-palladium alloys containing 5 and 10 at. % nickel.[1] The data indicated a broad impurity band of vibrations whose peak height increased with concentration. The position of the energy of the peak coincided with the estimate of the localized-mode frequency as determined from theory for a single substitutional impurity differing only in mass from the host atoms.

Recently, neutron scattering measurements have also been performed on other random binary alloys in a search for resonant modes of vibration[2] associated with heavy-mass solute atoms in dilute binary alloys.

Svensson, Brockhouse, and Rowe[3] reported measurements on single crystals of gold in copper where the dispersion curves of frequency versus wave vector of the vibrations were determined. Evidence for resonant modes of vibration can be indirectly obtained from the data using a recent theory of Elliott and Maradudin.[4] The theory is based upon assumptions of a dilute random binary alloy in which the solute atoms differ only in mass from the solvent atoms. Their theory shows that the phonons in the alloy should be shifted to lower frequencies and broadened in comparison to the phonons of pure copper. The shift and broadening of the phonons can be predicted from this theory where only a knowledge of the frequency distribution of the perfect crystal is required. The frequency of the resonant modes of vibration, according to the calculation should occur at the first zero in the frequency shift of the perturbed phonons. This resonant frequency obtained from the first zero in the frequency shift is also the resonant frequency predicted from theory for a single heavy-mass impurity. In the measurements on

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[2] R. Brout and W. M. Visscher, Phys. Rev. Letters **9**, 45 (1962); Yu Kagen and Ya. Iosilevkii, Zh. Eksperim. i Teor. Fiz. **44**, 1375 (1963) [English transl.: Soviet Phys.—JETP **17**, 925 (1963)].

[3] E. C. Svensson, B. N. Brockhouse, and J. M. Rowe, Solid State Commun. **3**, 245 (1965).

[4] R. J. Elliott and A. A. Maradudin, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965), Vol. I, p. 231.