center has been achieved.

It is expected that the ESR spectra from the other fluoride crystals (SrF_2, BaF_2, and CdF_2) can be analyzed with the same degree of accuracy as that obtained for the $CaF_2:Mn^{2+}$ system. It would be interesting to compare the various spin-Hamiltonian parameters, particularly those of the fluorine superhyperfine interactions, in an effort to investigate the detailed electronic structure of the manganese-fluorine complex MnF_8 for the various hosts.

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Temperature Dependence of Optical Absorption Lines from Iron Atoms in a Krypton Matrix[*]

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The optical absorption spectrum of iron atoms isolated in a krypton matrix contains two narrow lines at $\lambda = 3004 \pm 0.5$ and 2969 ± 1.0 Å. These lines are related to the two multiplet lines $3d^6 4s\ {}^5D_4\text{-}3d^7 (a\ {}^4F)4p\ {}^5D_4^\circ$ and $3d^6 4s^2\ {}^5D_4\text{-}3d^7(a\ {}^4F)4p\ {}^5D_3^\circ$. The linewidths (full width at half-maximum) at a matrix temperature of 4 K are 42 ± 1.5 and 38 ± 4 cm^{-1}, respectively. The lines are asymmetric (high-energy tail) and the linewidths increase with increasing temperature. From the line-shape analysis of the 3004 Å line at 4.2 and 20.5 K, the effective Debye temperature of solid krypton as probed by iron atoms is determined: The temperature dependence of linewidth yields $\Theta_D = 60 \pm 5$ K; the asymmetry of the line gives $\Theta_D = 53 \pm 6$ K.

Rare-gas matrix-isolated atoms have been studied in the last 20 years by optical absorption[1] and emission[2-4] spectroscopy. Until recently these studies have been confined to alkali-metal atoms or other metal atoms with total symmetric (S-state) ground states. Mann and Broida[1] have extended the optical absorption experiments to rare-gas matrix-isolated transition-metal atoms.

In most calculations made to account for the observed matrix-induced energy shifts of the absorption and emission lines from impurity atoms in rare-gas matrices (e.g., McCarthy and Robinson,[5] Brith and Schnepp,[6] Micklitz[7]), the interaction of the impurity atom with lattice motions has been neglected, i.e., the rare-gas solid has been treated as a static nondeformable lattice.

Zwanzig[8] has developed expressions for emission and absorption line shifts and for linewidths by using the same assumptions as McCarthy and Robinson[5] but with the additional consideration of the influence of lattice vibrations on the mean positions and widths of the lines. This analysis is a straightforward application of a theory developed by Lax[9] who calculated the shape of optical absorption and emission lines of impurity atoms in crystals with emphasis on the role of lattice vibrations. Lax shows, for example, that the second moments of optical absorption and emission lines should be proportional to the mean-square displacement $\langle x^2(T)\rangle$ of the impurity atom at the crystal temperature T. To the authors' knowledge until now no experiment has been reported in which the influence of temperature on absorption line position and line shape of impurity atoms in rare-gas matrices has been quantitatively measured.

Recently experiments on matrix-isolated atoms have been extended to Mössbauer studies on ^{57}Fe atoms in rare-gas matrices.[10–12] The recoilless fraction f of absorbed γ rays measured as a function of matrix temperature T gives information about the mean-square displacement $\langle x^2(T)\rangle$ of the ^{57}Fe atom in the rare-gas matrix $[\ln f \propto \langle x^2(T)\rangle]$. It is this point where there exists a connection between Mössbauer and optical absorption studies on impurity atoms in crystals.

The study of the temperature dependence of optical absorption lines from iron atoms in rare-gas matrices and the comparison of these results with that of the ^{57}Fe Mössbauer experiments offers a possibility to test the theory of Lax for an impurity iron atom in a rare-gas matrix. The optical absorption spectrum of iron atoms in an argon matrix has been found to be much more complex than the spectra in krypton and xenon matrices; the spectra in krypton and xenon matrices look similar.[1] In these experiments the krypton matrix has been selected to study the temperature dependence of iron absorption lines.

The apparatus used and the general features of sample preparation have been described elsewhere.[1] Mann and Broida[1] studied the absorption spectra of iron in rare-gas matrices at iron atomic concentrations of about 10^{-4}. Typical flow rates of matrix gas in these experiments were about 0.5 atm cm^3/min or a rare-gas deposition rate of about 1000 Å/sec for a sticking coefficient of 50%.

Mössbauer experiments on ^{57}Fe atoms in rare-gas matrices,[11,12] however, have shown that with such high deposition rates a broadening of the Mössbauer resonance absorption lines is observed. This broadening has been explained[11,12] by crystal imperfections which lead to noncubic crystalline fields at the iron-atom sites. The interactions of these fields with the ^{57m}Fe quadrupole moment produce line broadening. For high rare-gas deposition rates the surface diffusion time of the rare-gas atoms is reduced leading to the creation of a more dislocated environment and therefore to a broader Mössbauer resonance line. A similar broadening can be expected in the optical studies, since ill-defined crystalline environments (not cubic symmetry) give rise to additional crystal field splittings and in this way to extra line broadening.

For this reason the rare-gas deposition rates in these experiments have been considerably decreased to about 20 Å/sec. A lowering of the rare-gas deposition rate below this value gave a decrease in the intensity of the absorption lines. This might indicate that the surface diffusion time of the iron atoms becomes long enough to allow iron clumping. The deposition rates were determined in the beginning of sample preparation by measuring the time interval between the appearance of two interference rings produced by monochromatic light passing through the rare-gas layer.

TABLE I. Absorption-line positions λ_{Kr} ($\Delta\lambda = \pm 2$ Å) and linewidths (FWHM) of iron atoms in a krypton matrix at $T = 4.2$ K (iron atomic concentration 0.5%) together with the absorption lines of free iron atoms (λ_{gas}). Upper-state configurations and designations from Ref. 13. Ground-state configuration: $3d^6 4s^2\, a\, ^5D_4$ (Ref. 13). The linewidth values in parentheses are the values given by Mann and Broida (Ref. 1).

Configuration	Desig.	λ_{gas} (Å)	λ_{Kr} (Å)	$\nu_{\mathrm{Kr}}-\nu_{\mathrm{gas}}$ (cm)$^{-1}$	FWHM (cm)$^{-1}$
$3d^6 4s(a\,^4D)4p$	$x\,^5F_4^\circ$	2462.6	2429[a]	550 ± 30	200 ± 30
	$x\,^5F_5^\circ$	2483.3	2447	600 ± 30	250 ± 10 (652)
	$x\,^5D_3^\circ$	2501.1	2469[a]	500 ± 30	125 ± 25 (328)
	$x\,^5D_4^\circ$	2522.8	2490	520 ± 30	100 ± 10 (806)
	$y\,^5P_3^\circ$	2719.0	2684	480 ± 25	110 ± 5 (278)
$3d^7(a\,^4F)4p$	$y\,^5F_4^\circ$	2936.9	2890	550 ± 25	260 ± 20
	$y\,^5F_5^\circ$	2966.9	2920	540 ± 25	340 ± 20 (518)
	$y\,^5D_3^\circ$	2983.6	2969	165 ± 20	38 ± 4 (158)
	$y\,^5D_4^\circ$	3020.6	3004	175 ± 20	42 ± 1.5 (200)
$3d^6 4s(a\,^6D)4p$	$z\,^5P_3^\circ$	3440.6	3315	1100 ± 20	120 ± 10 (273)
	$z\,^5F_5^\circ$	3719.9	3575	1090 ± 20	310 ± 20 (392)
	$z\,^5D_3^\circ$	3824.4	3684	1000 ± 20	200 ± 30 (251)
	$z\,^5D_4^\circ$	3859.9	3725	940 ± 20	230 ± 20 (376)

[a] In the absorption spectrum measured by Mann and Broida (Ref. 1) these lines are either not given or not correlated to a transition in the free iron atom.

Table I, columns 4 and 6, gives the experimentally observed absorption lines [line position and full width at half-maximum (FWHM)] for iron in krypton matrices with iron atomic concentrations of about 0.5% and a matrix temperature of 4.2 K.

A correlation between these absorption lines and the absorption lines of free iron atoms[13] (Table I, column 3) was made by comparison of relative line positions and line intensities. The fine-structure splittings ($^5D_3$-$^5D_4$, $^5F_4$-$^5F_5$), for example, are almost the same for the matrix-isolated and the free iron atom. The relative line intensities I within one multiplet are reasonably close to the theoretical values following from an L-S coupling scheme[14]: $[I(^5D_4)/I(^5D_3)]_{\mathrm{expt}} = 3 \pm 0.5$ (theoretical value: 5); $[I(^5F_5)/I(^5F_4)]_{\mathrm{expt}} = 3.5 \pm 0.8$ (theoretical value: 7.36). The experimental values are averaged over all observed $^5D_3$-$^5D_4$ multiplets and $^5F_4$-$^5F_5$ multiplets. The optical data thus indicate that the orbital momentum L of the iron atom in the krypton matrix is unquenched and that J is a good quantum number. This fact has been very helpful in the analysis of the Mössbauer spectra of ^{57}Fe atoms in rare-gas matrices.[12]

The most striking features of this new absorption spectrum compared with that earlier measured by Mann and Broida[1] are the following: (i) Line positions are the same within experimental errors. (ii) Linewidths, however, have been considerably reduced. (In Table I the observed linewidths of Mann and Broida has been given in parentheses.) (iii) All lines which have been observed in the absorption spectrum of Mann and Broida but which could not be correlated to any known optical iron transition are not observed. These facts show that the lower rare-gas deposition rate indeed gives a better-annealed matrix with better-defined crystal sites for the iron atoms: Ill-defined crystalline environments will not change the mean positions of the absorption lines but will broaden the lines due to additional crystal field splittings. The additional lines observed in a high- but not in a low-deposition-rate experiment could be explained as the absorption lines of iron atoms on interstitial sites. These lines might be shifted in comparison to the absorption lines of iron atoms on substitutional sites. A confirmation of this annealing theory can be seen in the following: If the iron-doped krypton matrix is made with a high deposition rate (1000 Å/sec), but in addition the krypton layer is heated during the deposition by infrared radiation (tungsten light source), similar narrow absorption lines as in a low-deposition-rate experiment are observed.

Table I shows that the two multiplet lines $3d^6 4s^2\,{}^5D_4$-$3d^7(a\,{}^4F)4p\,{}^5D_4^\circ$ and $3d^6 4s^2\,{}^5D_4$-$3d^7(a\,{}^4F)4p\,{}^5D_3^\circ$ have the smallest matrix-induced energy shifts (~ 170 cm^{-1}) and also the smallest FWHM (~ 40 cm^{-1}) of all observed lines. It should be mentioned here that these are the narrowest lines which have been observed in the absorption spectra of impurity *atoms* in rare-gas matrices. All the other lines in Table I have larger energy shifts and are considerably broader. Since the crystal field splittings should be in first order proportional to the matrix-induced atomic level shifts, it is expected that this greater broadening is caused by unresolved crystal field splittings. In Lax's theory, however, the linewidths are caused by lattice vibrations only. For this reason the multiplet lines $3d^6 4s^2\,{}^5D_4$-$3d^7(a\,{}^4F)4p\,{}^5D_4^\circ$ and ${}^5D_3^\circ$ only are suitable for a test of Lax's theory. Since the ${}^5D_3$ line is a factor of 3 weaker than the ${}^5D_4$ line, the latter one has been selected to study the influence of temperature on line position and line shape.

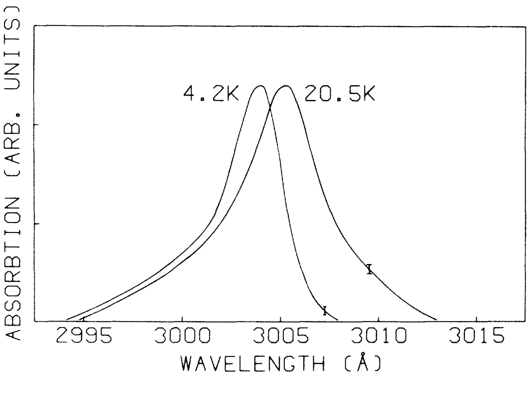

FIG. 1. $3d^6 4s^2\,{}^5D_4$-$3d^7(a\,{}^4F)4p\,{}^5D_4^\circ$ absorption line of iron atoms in a rare-gas matrix (iron atomic concentration 0.5%) at $T_1 = 20.5$ K and $T_2 = 4.2$ K. The spectral resolution is 0.5 Å. The error bars represent the noise contribution.

TABLE II. Line-peak position and the first three line moments of the $3d^6 4s^2\,{}^5D_4$-$3d^7(a\,{}^4F)4p\,{}^5D_4^\circ$ absorption line from iron atoms in a krypton matrix (iron atom concentration 0.5%) at two temperatures. The errors given for the line-peak positions $\lambda_{\max}$ ($h\nu_{\max}$) and mean line positions (first line moments $h\bar{\nu}$) are the errors in the relative line positions between $T_1 = 20.5$ K and $T_2 = 4.2$ K. The errors in the absolute line positions are ±0.5 Å (±5 cm^{-1}).

	$T_1 = 20.5$ K		$T_2 = 4.2$ K	
$\lambda_{\max}$	3005.2	±0.15 Å	3004.0	±0.15 Å
$h\nu_{\max}$	33266	±1.5 cm^{-1}	33279	±1.5 cm^{-1}
$\langle h\nu\rangle = h\bar{\nu}$	33274	±1.5 cm^{-1}	33296	±1.5 cm^{-1}
$\langle (h\nu - h\bar{\nu})^2\rangle$	1230	±60 cm^{-2}	770	±60 cm^{-2}
$\langle (h\nu - h\bar{\nu})^3\rangle$	14500	±2000 cm^{-3}	18500	±2000 cm^{-3}

Figure 1 shows the $3d^6 4s^2\,{}^5D_4$-$3d^7(a\,{}^4F)4p\,{}^5D_4^\circ$ iron absorption line in a krypton matrix (0.5% iron atomic concentration) measured at $T_1 = 20.5$ K and $T_2 = 4.2$ K with a spectral resolution of 0.5 Å. Since there are annealing effects which narrow the lines, the 4.2-K spectrum is observed after the 20.5-K spectrum. Table II gives the line-peak positions and the first three line moments at 4.2 and 20.5 K; these values are averaged values of several measurements.

The following temperature effects are observed: (a) There is a red shift of the line-peak position when the matrix temperature is increased from 4.2 to 20.5 K. (b) The linewidth (second moment) increases with increasing temperature. (c) There is an asymmetry or skewness in the line shape; the high-energy tail produces a nonzero third moment. Both the increasing linewidth with increasing temperature and the line skewness have been predicted by Lax. This skewness is a typical quantum-mechanical effect and has its origin in the Stoke rule which states that it is easier to emit a phonon than to absorb one by the ratio of $(\bar{n}+1)/\bar{n}$, where $\bar{n}$ is the average number of phonons involved in the process. On absorption of light this favors the absorption of a higher-energy photon which results in the observed high-energy tail of the absorption line.

The ratio of the second moments of absorption lines at the temperatures T_1 and T_2 is given by Lax as

$$\langle (h\nu - h\bar{\nu})^2 \rangle_{T_1} / \langle (h\nu - h\bar{\nu})^2 \rangle_{T_2} = \langle x^2(T_1) \rangle / \langle x^2(T_2) \rangle \ , \tag{1a}$$

where $h\bar{\nu} = \langle h\nu \rangle$ is the first moment of the absorption line and $\langle x^2(T) \rangle$ is the mean-square displacement of the impurity atom in the host lattice at the temperature T. By assuming a Debye model for the frequency spectrum with which the oscillations of the iron atom in the rare-gas matrix can be described, $\langle x^2(T) \rangle$ can be written as[15]

$$\langle x^2(T) \rangle \sim 1 + 4 \left(\frac{T}{\Theta_D} \right)^2 \int_0^{\Theta_D/T} \frac{x}{e^x - 1} \, dx \ , \tag{1b}$$

where Θ_D is the Debye temperature ($k\Theta_D = \hbar\omega_D$).

The ratio of the third to the second line moment at the temperature $T = 0$ as given by Lax (written in the Debye approximation) is

$$[\langle (h\nu - h\bar{\nu})^3 \rangle / \langle (h\nu - h\bar{\nu})^2 \rangle]_{T=0} = \tfrac{2}{3} \hbar\omega_D \ . \tag{2}$$

The analysis of the data in Table II gives for Θ_D by using formulas (1a) and (1b), $(\Theta_D)_1 = 60 \pm 5$ K and by using formula (2), $(\Theta_D)_2 = 53 \pm 6$ K. These values have to be compared with the Θ_D value obtained from Mössbauer experiments on ^{57}Fe atoms in a krypton matrix: $(\Theta_D)_{\text{Mössbauer}} = 55.8 \pm 4$ K.[12]

This good agreement between the Θ_D values obtained from such totally different experiments shows that Lax's theory indeed can be applied to the analysis of absorption line shapes of impurity atoms in rare-gas matrices; it shows further that an additional line broadening of the $3d^6 4s^2 \, {}^5D_4$-$3d^7 (a\, {}^4F) 4p \, {}^5D_4^\circ$ iron line due to unresolved crystal field splittings is negligible.

The observed temperature-induced red shift of the absorption line can be interpreted in different ways. In Lax's theory a shift in the line position can be caused if (i) in the formula for the energy shift due to the interaction of the impurity atom with the lattice motion a quadratic term in the lattice displacements q_j is added, or (ii) the coupling constants between the energy states of the impurity atom and the lattice motion are temperature dependent due to the lattice expansion with temperature. In either case the formulas (1a) and (2) would be modified.

O'Rourke[16] and later Meyer[17,18] extended Lax's theory. They obtain a shift in the mean position of the absorption line with temperature by considering a small change in the lattice frequencies which accompanies the photon-induced electronic transition. Such a change in the lattice frequencies does not effect the line shape obtained by Lax, i.e., all moments higher than the first are unchanged and formulas (1a) and (2) would not be modified.

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