Efficiency of crystalline laser materials based on lanthanides

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Abstract : Lanthanide-based laser-crystal efficiency has been investigated, using the laser-active ions Dy^{3+} and Nd^{3+} as significant illustrations. Our calculations, and various approaches by other authors, are reviewed. In specific examples of our treatment, the analytical self-consistent field (SCF) expansion method has been used to calculate accurate *ab initio* wave functions and energy levels for a number of excited states of Nd^{3+} and Dy^{3+}, which were investigated for the first time. General group-theoretical principles were considered and the formulae for crystal-field parameters were obtained. The Racah quantum numbers were included in these calculations, in fact showing sizeable energy effects. Our oscillator strengths, calculated from the SCF wave functions, revealed which orbitals can be neglected without influencing the transition probability at the fourth significant figure. The relationship to the spectral character of the pumping device was considered. The efficiency parameters (mechanical, economic, and energetic) have to be considered as supplementing the related threshold energy parameter. It would be conceivable to predict the applicability of competing laser systems to a specific task, based on integrated energy pictures.

Keywords : Laser-active lanthanides, analytic SCF method, excited states of Nd^{3+}, Dy^{2+}.

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I Introduction and history

Our purpose here is to highlight our investigations involving both theoretical and engineering considerations relative to the efficiency of solid-state crystalline laser materials, and to suggest major goals for the immediate future in this field. Crystalline laser materials have well defined internal structure, which permits the use of generalized theoretical methods in identifying the most promising combinations of host lattice, laser-active ions, and the associated parameters, for experimental investigations. This cuts down the cost of extensive experimental searches for effective and efficient laser materials. Also, a better understanding of the role of the host-ion interaction is achieved, and such information is applicable

as input to further investigations of solid-state polycrystalline and/or glass lasers. We look into these material systems as broadly as is practical in order to integrate the important contributions from areas as diverse as theoretical physics and electronic engineering.

The cornerstone of our investigations is the method of atomic analytic self-consistent fields (SCF) (Roothaan and Bagus 1963). We have produced analytical SCF calculations which are the most accurate available. Our calculations are the first for excited configurations with two and three open shells of different symmetries. Concerning lanthanides, the Racah quantum numbers were included for the first time. (Synek and Ramirez 1969, 1980) ; (Synek *et al* 1979) ; (Synek 1990).

Also, there are interesting approaches of other authors to the lanthanide problem (Carnall *et al* 1989), (Sardar *et al* 1989), (Cunningham 1989).

2. Accuracy of the calculations

We subject our analytical SCF calculations to several accuracy criteria before results are released for publication.

These criteria are :

(a) Constancy of the calculated total energy to eight significant figures, even after repeated basis-function exponent optimization according to the variation principle, if accurate SCF is desired.

(b) Maximum permissible SCF convergence threshold smaller than 0.001.

(c) The virial theorem to be satisfied to at least five significant figures.

(d) The cusp condition to be satisfied either identically or to an adequate number of significant figures for the individual orbitals.

(e) Elimination of the wobbling at the tail of the radial orbitals to more than three decimal places, as long as it is dictated by the optimization based upon the variation principle.

(f) Comparison with numerical technique SCF calculations wherever they are available. These are not usually available for excited states and for many important ions.

We address a possible argument concerning the validity of criterion (e). Namely, the tail of the Hartree-Fock orbitals cannot be described by a single negative exponential, but requires a functional linear combination of negative exponential, but requires a functional linear combination of negative exponentials (except for the *s*-symmetry). Then one might obtain some wobbling at the very distant tail of the orbitals even for ideal Hartree-Fock orbitals. However, we are interested in the first three to four decimal places in the radial wave functions.

Beyond that computational effects inherent in analytical expansions and "physical" correlation and relativistic effects far overshadow more accurate hypothetical values in the ideal Hartree-Fock treatment. Yet we are seeking maximum possible accuracy to four decimal places. Experience shows that repeated optimization, based upon the variation principle, can eliminate wobblings to at least three decimal places. Experience also shows that wobblings can become exceedingly large if one used a minimum number of basis functions in the expansion, as is required only by the orthogonality of the orbitals. If, however, one uses a saturated basis set of functions, the total energy improves significantly, together with a decrease in tail wobblings. Hence we conclude that elimination of orbital tail wobblings is justified.

3. Lanthanide wave functions

Our group had produced earlier the most accurate analytic SCF wave functions attainable for the ground state and many important excited states of the lanthanides Ce^{3+}, Nd^{3+}, Pr^{3+}, and Dy^{3+}. In selecting the excited states in our calculations, we considered their participation in laser transitions, or in the pumping process, or whether their symmetries indicated they could contribute through configuration interaction to the ground or excited states of importance.

Such calculations were never done before. Only for the $4f$ orbitals of the ground states of lanthanide ions had approximate orientational calculations of the wave functions have been previously published, with the exception of our earlier intermediate basis set calculations for Pr^{3+} and Nd^{3+} ; later, accurate wave functions were obtained for these ions, as was mentioned above.

Calculations were carried out *ab initio*, without introduction of any nonfundamental empirical parameters. Comparison with experimental data was done where possible. Such comparisons lead us to the estimation of correlation energy differences. However, we calculated spectroscopic states, not yet measured. Such calculations provide useful interpretations or predictions in atomic spectra. Since the emission spectra of the free ions of lanthanides are difficult to analyze, theoretical calculations of energies are essential. Our wave functions also provide a sound basis for the theoretical interpretations of the spectra of lanthanide ions in general (Wybourne 1965) ; (Fano and Racah 1959).

4. Lanthanide ions and crystal lattices

Our atomic analytical SCF wave functions were important for our investigations of lanthanide ions inserted in the potential fields of crystal lattices of various symmetries. Applications of accurate analytical SCF wave functions (Synek and Grossgut 1970, Wakim *et al* 1972) to different crystal-field models were used to compute crystal-field parameters (CFP) for the laser-active material Nd^{3+} : CaF_2. Inter-

dependences between these and other energy significant parameters, including energy perturbation of the ground state of Nd^{3+} when inserted into the potential field of cubic CaF_2, were explored and comparisons made with available theoretical and experimental data. Comparison is needed due to unexplained discrepancies between approaches (Rampton 1974). An Nd^{3+} ion in a crystalline salt is situated in a potential $V(r)$, the crystalline field, which arises from the charges eZ_1 on neighbouring ions at positions R_1. Approximating the crystal ions by point charges we have :

$$V(r) = \sum_i \frac{eZ_1}{|r - R_i|}.$$

(Vectorial quantities, etc., are automatically to be understood, where appropriate, throughout this article). This potential partially lifts the $2J + 1$ fold degeneracy of the multiplet levels of the free Nd^{3+} ion. From susceptibility measurements, we see that these splittings due to $V(r)$ smaller than the multiplet separations, so that mixing of different multiplets can usually be neglected. The rare earths differ from the transitions metal elements where crystal-field splittings are greater than those of the multiplets. The smallness of the splittings for the rare earths is due to the $4f$ electrons being shielded from $V(r)$ by the outer electrons and to the ions being well separated. The number of new levels depends upon the symmetry of the crystal field, there being fewer levels the higher the symmetry. For most lanthanide salts the symmetry is relatively low, but by introducing lanthanide ions into other host lattices such as cubic CaF_2, the effects of higher symmetries can be investigated. There are two general group-theoretic rules which are valuable in investigating the lowest energy level structure of lanthanide ions in crystals. These are :

(a) Kramers' theorem :

In the absence of an applied magnetic field the levels of an ion with odd number of $4f$ electrons can at most split into levels which are doubly degenerate. This applies to lanthanides with half integral J ground states, e.g., Nd^{3+}.

(b) John-Teller effect :

The environment of an ion with a degenerate ground state, Kramers' doublets excepted, spontaneously distorts to a lower symmetry so as to remove the degeneracy. It implies that ions with an even number of $4f$ electrons always have singlet ground states, e.g., Dy^{2+}.

If we assume that the $4f$ electrons do not overlap neighbouring ions, then $V(r)$ satisfies Laplace's equation and can be expanded in spherical harmonics :

$$V(r) = \sum_l \sum_{m=-l}^{l} A_l^m r^l Y_l^m(r) = \sum_{l,\,|m| \leq l} V_l^m$$

where, for the point charge model,

$$A_l^m = \sum_j \frac{4\pi}{2l+1} \frac{Z_j}{R_j^{(l+1)}} (-1)^m Y_l^{-m}(R_j).$$

For a $4f^n$ configuration the potential energy is written :

$$\sum_i V(r_i) = V_o.$$

The number of terms in V is restricted by symmetry as follows :

(a) If the z-axis is an m-fold rotational axis then V_o contains $V_l m$.

(b) If there is a center of inversion, there are no odd l terms, as for CaF_2.

Further simplification comes when matrix elements $\langle 4f \mid V_o \mid 4f \rangle$ are computed. The resulting integrals are :

$$\int d\tau \psi_{4f}^* r^l V_l^m \psi_{4f}$$

and the radial integrals $\langle r^l \rangle$ factor out. Since

$$\psi_{4f} \propto V_3^\xi,$$

the angular integrals are :

$$\int dv (V_3^\xi)^* V_l^m V_3^{\xi'} \sin \nu,$$

and these vanish unless $l \leq 6$.

In evaluating matrix elements of V_c between multiplet states $\mid J, M_J \rangle$ the angular integrations are most readily achieved by the method of operator equivalents (Taylor and Darby 1972). For a given multiplet the matrix elements of V_c are proportional to those of "equivalent" operators containing J_x, J_y, and J_z in place of x, y, and z, respectively, in the point charge model. Following Hutchings' notation (Hutchings 1964) for the operator equivalent crystal-field Hamiltonian

$$\hat{H}_o = \sum_{l, m} B_l^m O_l^m,$$

where the B_l^m's are related to the CFP's through

$$B_l^m = A_l^m \langle r^l \rangle \Theta_l,$$

where

$$\Theta_2 = \alpha_J, \quad \Theta_4 = \beta_J \text{ and } \Theta_6 = \gamma_J$$

are proportionality constants which need only be calculated once for a given lanthanide ion. Hutchings (1964) tabulated the matrix elements for all operators between states $\mid J, M_J \rangle$, for constant J, appropriate to the lanthanides. These tables enabled us to build the energy matrix and perform the energy level computation.

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A point charge model might suffice for *relative* energy shifts (4f shielded). Point charge models appear reasonable in spite of the fact that they are a relatively simple approximation.

The resulting Hamiltonian associated with a general cubic crystal lattice is :

$$\hat{H}_o = B_4^o . \left[O_4^o + 5.0_4^4 \right] + B_6^o . \left[O_6^o - 21.0_6^6 \right],$$

where O_m^n are expressed in terms of the angular momentum operators J_x, J_y, and J_z (Taylor and Darby 1972). To obtain a more extensive comparisons, two point charge models for cubic CaF_2 were employed. The difference between the CFP's using the two models, was due to the different assignment of Z_{eff} to the Nd^{3+} ion in each model. Likewise, these CFP's when compared to results obtained by other, differed by $\sim$ 15% due to their use of model-dependent free-ion wave function. Point charge models ignore bonding, shielding and overlaps which had been considered by others. In addition, MO theory accounted for covalency effects. None of the above was in better agreement with reliable experimental data than our results.

The general expression for Stark splitting eigenvalues of cubic $\hat{H}_o$ can be shown to be :

$$\Delta E_0 = a.B_4^o + b.B_6^o,$$

where a and b are real numbers. The energy shift experienced by the unperturbed ground state multiplet of Nd^{3+} when inserted in the potential field of cubic CaF_2 was shown (Synek and Schultz 1978) to be $\sim 10^{-5}$ a.u. (Hartree) and justifies our free-ion wave functions in further calculations associated with $Nd^{3+} : CaF_2$.

The ratio B_4^o/B_6^o is useful in studying the ground state of lanthanide ions ; the parameter, x, is easily defined as :

$$B_4^o/B_6^o = (x/(1- \mid x \mid)). (F(6)/F(4)). \quad \text{where} \mid x \mid \langle 1.$$

our values of x, for the ground state $^4I_{9/2}$ of Nd^{3+}, agree very well with those of other groups (Synek and Schultz 1978). — (Some properties of crystalline laser materials based on Nd^{3+} are summarized in Table 1).

5. Efficiency and laser materials based on lanthanides

In our investigations of the efficiency of solid-state laser materials the problem of matching the emission spectrum of a suitable pumping lamp with the absorption spectrum of a specific crystal has been of enormous importance. Initially, in order to design a pumping lamp for a particular crystalline laser material, the perturbation of the absorption spectrum of the laser-active ion by the crystal-field potential is to be examined in detail. For the rare earths a

Table I. Some properties[a] of crystalline laser materials based on Nd^{3+}.

Host lattice	τ (10⁻⁶ sec)	σ (10⁻¹⁹ cm²)	Refractive index	λ_L (10⁻⁶ m)	Threshold (J)	Temp. (K)	Mode	Hardness	Symmetry
CaF_2	1160	—	1.43	1.046	60	77	P	4.0	Fm3M
SrF_2	1150	—	1.43	1.037	480	300	P	4.0	Fm3m
BaF_2	—	—	—	1.06	1600	77	P	—	—
YAG[b]	210	4.6	1.83	1.0648	0.13	300	CW	8.5	Ia3d
CeF_3	385	—	1.62	1.0638	41	90	P	4.5	—
$CeCl_3$	175	25.0	—	1.065	0.06	300	CW	—	—
LaF_3	700	0.4	1.58	1.0633	150[c]	300	P	4.5	P$\bar{3}$cl
				1.0631	93[c]	77	P		
				1.0399	75[c]	77	P		
				1.0407	17[f]	300	P		
				1.0633	42[d]	300	P		
				1.0403	8[d]	77	P		
				1.0407	—	300	CW[e]		

[a] τ : radiative lifetime ; σ : cross section ; λ_L : laser wavelength ; — : data unavailable
[b] Keith and Roy (1954)
[c] Johnson (1963)
[d] Dmitruk and Kaminskii (1968)
[e] Voron'ko et al (1968)

complex situation arises concerning the complete classification of their electronic states. This was attacked by the theory of irreducible tensors (Fano and Racah 1959) ; and, particularly, by Racah quantum numbers ν and $U = U\,(u_1,\ u_2)$. The calculation of crystal-field parameters for excited states of lanthanide ions labeled by such quantum numbers leads to clearer insight into the energy significance of such states and indicates whether even more complex substates may merit attention.

The laser-active ion Dy^{2+} is of technical interest ; one of the earlier magnetically tunable solid-state lasers utilized Dy^{2+}. We calculated, using analytical SCF wave functions, (Synek and Ramirez 1980), the average values of the radial moments $\langle r^n \rangle_{4f}$ for excited $4f^{10}$ states of Dy^{2+}. These results, useful in determining many physical parameters, were classified by Racah quantum numbers as referred to above, and appear in Table 2.

Table 2. Average values of $\langle r^n \rangle_{4f}$ (a.u.), ($n = 3, -1, 0, 1, 2, 4, 6$), for the ground and excited states of the Dy^{2+} ion, using Racah quantum numbers.

State[a]	$\langle r^{-3} \rangle$	$\langle r^{-1} \rangle$	$\langle r^0 \rangle$	$\langle r^1 \rangle$	$\langle r^2 \rangle$	$\langle r^4 \rangle$	$\langle r^6 \rangle$
$4f^{10}, 4\ ^1F\ (21)$	9.702	1.632	1.000	0.797	0.824	1.811	8.874
$4f^{10}, 4\ ^1H\ (21)$	9.727	1.635	1.000	0.795	0.817	1.772	8.541
$4f^{10}, 4\ ^1H\ (22)$	9.686	1.630	1.000	0.799	0.827	1.834	9.059
$4f^{10}, 2\ ^3F\ (10)$	9.697	1.631	1.000	0.798	0.825	1.619	8.938
$4f^{10}, 4\ F\ (10)$	9.729	1.635	1.000	0.795	0.817	1.767	8.504
$4f^{10}, 4\ ^3F\ (21)$	9.721	1.634	1.000	0.795	0.818	1.780	8.607
$4f^{10}, 4\ ^1F\ (30)$	9.732	1.635	1.000	0.794	0.816	1.764	8.477
$4f^{10}, 2\ ^3H\ (11)$	9.699	1.631	1.000	0.798	0.825	• 1.817	8.922
$4f^{10}, 4\ ^3H\ (11)$	9.728	1.635	1.000	0.795	0.817	1.770	8.522
$4f^{10}, 4\ ^3H\ (21)$	9.725	1.634	1.000	0.795	0.817	1.773	8.554
$4f^{10}, 4\ ^3H\ (30)$	9.726	1.634	1.000	0.795	0.818	1.777	8.587
$4f^{10}, 4\ ^3M\ (30)$	9.739	1.636	1.000	0.794	0.814	1.751	8.364
$4f^{10}, 4\ ^5S\ (00)$	9.766	1.638	1.000	0.792	0.811	1.746	8.447
$4f^{10}, 4\ ^1D\ (20)$	9.735	1.635	1.000	0.794	0.816	1.773	8.654
$4f^{10}, 4\ ^5G\ (20)$	9.758	1.637	1.000	0.793	0.812	1.738	8.249
$4f^{10}, 4\ ^1I\ (20)$	9.772	1.639	1.000	0.791	0.806	1.704	7.982

[a] States are labeled as : $4f^{11}, \nu\ ^{2S+1}L(u_1, u_2)$.

[b] The ground states of $\langle r^n \rangle_{4f}$ (a.u.), ($n = -3, 2, 4, 6$), for various lanthanide ions, are listed by Wakim et al (1972).

Theoretical determination of physical parameters, employing SCF wave functions, has become routine (Synek and Ramirez 1969) ; our calculations of $\langle r^n \rangle_{4f}$ for excited states of Dy^{2+} were the first. We often found Racah quantum numbers to be as important as angular momentum quantum numbers. Particular $\langle r^n \rangle_{4f}$ values of interest and the associated physical parameters were :

$n = -3$;   the spin-orbit interaction as well as nuclear charge penetration effects.

$n = -1$;   electrostatic interaction energy of the electrons with the nucleus as well as the mutual electrostatic repulsion energy of the electrons.

$n = 0$;   normalization constant for the SCF wave functions.

$n = 1$;   the average radius of the electronic orbitals.

$n = 2, 4, 6$; the crystal-field parameters.

Ground state values of $\langle r^n \rangle_{4f}$ were available for comparison as we had performed these calculations (Wakim et al 1972). Excited state radial averages for $n = -3$, -1 and 2 differed by 1% whereas $\langle r^4 \rangle_{4f}$ and $\langle r^6 \rangle_{4f}$ values showed as much as 10% difference between excited states. This shows the energetic significance of Racah quantum numbers in calculations of crystal-field parameters. The results are particularly important as they suggest a correction for the crystal-field parameters as follows : it was emphasized that first-order perturbation theory is a good approximation, while second-order perturbation theory predicts that the ground state as well as the next excited states should be mixed when the crystal-field parameters are determined (Fano and Racah 1959). By mixing ground and excited states one expects improvement in the accuracy of theoretical calculations of crystal-field parameters by up to 10%. But, comparative data do not exist for the states of Dy^{2+} from other sources (or for any comparable lanthanide ion) concerning our results.

Due to indication of the energetic significance of states labeled by Racah quantum numbers, one can define new quantum numbers by using the theory of irreducible tensors to investigate the possible usefulness of substates labeled by such a new scheme.

We investigated the effects of a crystalline environment on a laser-active ion due to the two major computational methods, semi-empirical and *ab initio*. Variation of empirical parameters was successful in interpreting rare earth spectra in crystals. But it is correlative data processing and has only uncovered patterns without shedding light on the fundamental nature of the observed processes. This class of methods also has the inherent uncertainty associated with the interpretation of phenomena which used experimentally derived parameters as a foundations. Care must be exercised in assumptions made, in order to avoid insidious errors. As yet *ab initio* calculations are more restricted with respect to inclusion of a wide range of variables, which is to be expected due to the complexity of interdependence between all parameters. However, results obtained by *ab initio* methods are usually as good as parametric variation methods and give more

fundamental information (Synek and Schultz 1978) about the processes under consideration. In fact, the sensitivity of specific interactions is often clarified through their inclusion in *ab initio* calculations.

In general, the usefulness of our analytical SCF wave functions is supported by their applications and by citations in publications of other authors. This usefulness encourages the future use of our wave-functions for more complicated systems. Hence, one can use wave-functions for important states of various lanthanide ions for several applications, such as *ab initio* interpretation of existing semi-empirical results, e.g., for intermediate coupling energy levels. Applications are foreseen : configuration interaction effects (Rajnak 1965) on "free ion" energy levels ; supplementing data to matrix elements of spin-spin interaction (Reilly 1968) for various f-electron configurations ; intra-atomic magnetic interactions (Judd et al 1968) for any f^n ; other problems, using operator techniques and second quantization ; and relativity (Synek 1964). Calculations of oscillator strengths of lanthanides is facilitated by our simplifying rule concerning large determinants representing wave-functions, as it tells us which orbitals can be neglected when constructing Slater determinants, without influencing the calculated oscillator strengths at the fourth significant place. Without a simplifying rule it would take too much computer time to evaluate matrix elements involving products of determinants, each about 60×60 for a typical lanthanide ion transition. However, much less computer time is involved for transitions dealing with approximately 30 outer electrons (i.e., evaluating products of determinants where each determinant is constructed of 30 spin-orbitals).

6. Certain specific considerations in relation to efficiency   .

In the past, many expressions for calculating laser efficiency appeared but individual parameters in most cases do not appear in the literature for any two systems. Clearly, this makes initiation of efficiency comparisons difficult at best ; a data base must be compiled before any search for efficient laser solids is begun regardless of whether the search is to be theoretical and experimental in nature. Furthermore, many parameters in these expressions are left unrestricted and often degrade efficiency with little indication of the source or even the existence of degradation. It seems reasonable to investigate the behaviour of each parameter with respect to efficiency before attempting to optimize a complex function of interrelated variables. This approach is limited as parameters cannot be considered completely independently without loss of credibility. Also, unfortunately, there is a definite correlation between energy efficiency and cost efficiency which must be considered. Operationally related parameters must also be kept in mind since a component of a laser system may appear to be efficient with respect to energetic parameters while associated mechanical variables may reduce applica-

bility or raise long term maintenance costs to the point where it is virtually useless. For example (Singh et al 1975) Nd^{3+} : $CeCl_3$, remarkably energy efficient and useful in communication applications, is worthless for high power applications due to its softness and hygroscopic properties.

We systematized initial physical data by organizing a comparative survey of the literature centered around the laser-active system (Nd^{3+} : LaF_3 ; $^4F_{3/2} \rightarrow {}^4I_{11/2}$), but the goal was to acquire expertise needed to compile a larger body of data from which to begin an efficiency analysis. Data compiled in this search are summarized in Table 1. From this we attempted to organize the information so that patterns of efficiency contributions and interactions appeared (Synek and Schultz 1979).

Maximum luminescence in the Nd^{3+} : LaF_3 system is achieved with a doping concentration of 1.2% wt. of Nd^{3+} ions (Voron'ko et al 1968) ; at this concentration the mean lifetime of the metastable state is about 500 ξ sec as compared with the lifetime of 700 ξ sec for the radiative lifetime in Table 1 (Thornton et al 1969). The difference in parameters for Nd^{3+} : LaF_3 is probably due to variations in doping concentrations. A shorter lifetime leads to a decrease in threshold energy, if the pump pulse width is not comparable with radiative decay time. This discrepancy, in the lifetime of Nd^{3+} : LaF_3, may contribute to the disagreement, with respect to threshold energies, between sources as footnoted in Table 1. That Nd^{3+} : CeF_3 is lattice sensitized through the Ce^{3+} ion together with the isomorphous relationship between CeF_3 and LaF_3 leads to an interesting observation. When 1 wt. % Nd^{3+} : LaF_3 is further doped with 4 wt. of Ce^{3+} the absorption bands of the crystal are broadened by $\sim$ 11% and dipole-dipole sensitizing between Ce^{3+} and Nd^{3+} is observed (Skorobogatov and Azarov 1968). Ce^{3+} is the only trivalent lanthanide ion where such sensitizing has been observed in Nd^{3+} : LaF_3.

Most excitation to the $^4F_{3/2}$ level of Nd^{3+} is due to a cascade effect from higher energy levels, since the strongest absorption bands of Nd^{3+} : LaF_3 are of much higher energy than the position of the metastable state relative to the ground state. Most of these transitions are of the forbidden 4f-4f type, occurring between 12,000 and 20,000 cm^{-1}, so the absorption peaks Nd^{3+} : LaF_3 are weak and quite sharp (Dmitruk and Kaminskii 1968) ; (Zlenko et al 1971) ; unfortunately this is true in general, for rare earth laser materials. This makes the matching of output spectra of the pumping device with rare earth absorption bands of high priority with respect to efficiency. Such matching could be accomplished by laser excitation but this is usually costly and often requires a strong energy source which degrades the system. Success has been achieved by the use of semi-conductor lasers as pumping devices but they are not applicable to highpower output lasers. High pressure xenon-krypton lamps were efficient during prolong

pulse operation and give a fair spectral match with Nd^{3+} : LaF_3 (Mnuskin *et al* 1975). The better spectral overlaps found so far involve water-cooled mixed metal-halide lamps ; one of the best for Nd^{3+} : LaF_3 contains a mixture of Xe, Hg, NaI, and TlI. Safety considerations, due to the highly toxic thallium, could make this lamp expensive, but, in view of the energy efficiency and excellent spectral overlap properties of the lamp, this cost may have no effect on system applicability. Another aid to pumping performance is the use of a sensitizing ion such as the crosspumping due to Ce^{3+} mentioned earlier. This practice is common, yet, to date, the specific sensitizing ion or set of ions best suited for a particular crystalline material must be chosen mostly by trial and error since accurate analytic SCF wave functions have not yet been applied to such a predicting process.

For long range efficiency, cryogenic operation has significant potential for system degradation. Therefore, laser materials which can operate with minimum energy devoted to cooling are potentially the most useful ; in particular, materials that are laser-active at or above $300°$ K, are of first interest as potentially viable. The Nd^{3+} : LaF_3 system (Voron'ko *et al* 1968) emits in CW mode at $300°$ K with a water-cooled laser rod. In addition, excess heat generated in the cavity can be used to reduce the threshold energies significantly and thereby reduce the energy drain due to cooling. At $360°$ K a line appears ($\lambda_L = 1.0594\xi$) never observed at lower temperatures in Nd^{3+} : LaF_3. Further, at $480°$ K this and the 1.0633ξ line both reach minima in threshold energies of $12J$ and $18J$, respectively. Heat sensitizing yields a 57% drop in threshold energy compared to $300°$ K. Heat loss could also be reduced by using a sealed system filled with xenon, specific heat 0.0378 cal/g, under low pressures. Continuous evacuation would, in the long term, be quite impractical. We observed that low index of refraction, n, is correlated with laser output at shorter wavelengths ; efficiency is improved, since, with a lower index, there are fewer losses to the cavity due to the smaller angle of refraction. In this way, the losses in softer host crystals due to mechanical imperfections in the end planes, are partially compensated. By using a simplified version of the expression for the pumping threshold for pulsed mode 4-level laser system (Kaminskii *et al* 1973),

$$T_P(n) = A(nB + C),$$

where C can be ignored for temperatures below $\sim 500°$ K, it is evident that, in pulse mode, the pumping threshold is linearly related to the index of refraction. However, during continuous wave operation, the minimum power required to maintain the critical population inversion depends greatly on the round trip loss in the resonator (Finley and Goodwin 1963). In this case, contribution by the index of refraction is negligible. The variables A and B contain other parameters but contribution due to the index of refraction was the only one of interest here, so all

others were held constant. Also, the absorption line strengths of a material system are degraded by the rather sensitive factor $9n/(n^2+2)^2$. Line strength degradation, due to the index of refraction, in Nd^{3+} : YAG and Nd^{3+} : LaF_3 are 0.575 and 0.703, respectively, so a high index of refraction is beneficial assuming crystal strength is sufficient for good mechanical construction. This balance concerning threshold energy and absorption line strengths makes the acceptable range of indices of refraction quite narrow. The index of refraction predominantly manifests itself in macroscopic properties and its detailed connection to the host-ion interaction is not understood. This lack of clarity between macroscopic properties is a common problem in dealing with most efficiency-related parameters ; investigations with geometrically well-defined crystalline structures could clarify some of these relationships.

7. Conclusion

From the above discussion, it is apparent that the threshold energy, usually taken as the parameter of top priority, can be misleading unless the related efficiency parameters (mechanical, economic, as well as energetic) are considered. With an *intergrated picture* of the main parameters of systems relative to output performance, it would be conceivable to predict the applicability of competing laser systems to a specific task.

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