

Spin-Wave Spectrum of the Antiferromagnetic Linear Chain

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The methods of Bethe and Hulthén are used to build spin-wave states for the antiferromagnetic linear chain. These states, of spin 1 and translational quantum number k , are eigenstates of the Hamiltonian $H = \sum_j \mathbf{S}_j \cdot \mathbf{S}_{j+1}$ with periodic boundary conditions. For an infinite chain, their spectrum is $\epsilon_k = (\pi/2) |\sin k|$, whereas Anderson's spin-wave theory gives $\epsilon_k = |\sin k|$. For finite chains it has been verified by numerical computation that these states are the lowest states of given k , but no rigorous proof has been given for an infinite chain.

I. INTRODUCTION

THE problem of determining the ground state and the lowest excited states of the Heisenberg Hamiltonian for an antiferromagnet is of great physical interest but is very difficult to solve exactly in three dimensions. Consequently, it is useful to consider the more tractable case of the antiferromagnetic linear chain, which can serve as a check on approximations to the general case and may also, in certain crystals, approach the actual physical situation. The eigenstates of the nearest-neighbor Heisenberg Hamiltonian,

$$H = \sum_j (\mathbf{S}_j \cdot \mathbf{S}_{j+1} - \frac{1}{4}), \quad (1)$$

for a chain of N atoms with periodic boundary conditions have been studied by Bethe¹ and Hulthén.² They have proposed a solution for the antiferromagnetic ground state and calculated its energy for an infinite chain.

In this paper we consider the spin-wave excitations from this ground state, defining them as the lowest energy eigenstates of H corresponding to a given translational quantum number k . We specify the form of these states and calculate their energy spectrum as a function of k for both finite and infinite chains using the methods of Bethe and Hulthén. In order to make our results as convincing as possible, we proceed systematically from the case of short chains, where all the eigenstates can be calculated explicitly, to longer chains where this would be impractical. Each assumption, as it is introduced, is verified for shorter chains, and the final results are seen to be extremely reasonable.

II. SPIN-WAVE SPECTRUM FOR SHORT CHAINS (APPLICATION $N=6$, $N=8$)

In order to find the rigorous spin-wave spectrum for short chains, it is necessary to calculate the energy of the eigenstates and also their quantum numbers S (total spin) and k . The value of k corresponding to an

eigenfunction Ψ is defined by the relation

$$T\Psi = e^{ik}\Psi, \quad (2)$$

where T is the operator translating the entire chain through one lattice spacing. The spin-wave state of wave number k is taken to be the lowest energy state of quantum number k . We expect these spin-wave states to have spin 1. It is convenient to plot their excitation energy ϵ above the ground state as a function of $q = k - k_0$, where k_0 is the value of k associated with the ground state ($k_0 = 0$ if $N/2$ is even; $k_0 = \pi$ if $N/2$ is odd). For chains of 6 and 8 atoms Mattheiss³ has given the quantum numbers of all the states, and, in agreement with his results, we plot in Fig. 1 and 2 the spin-wave spectrum for these chains.⁴ All these states do indeed have spin 1.

III. SPIN-WAVE STATES AND BETHE-HULTHÉN STATES (APPLICATION $N=16$)

It is rather lengthy to compute all the states for chains with more than 10 atoms, and, therefore, it would be useful to find a method of selecting from among all the states the particular spin-wave states we wish to consider. A classification of the eigenstates

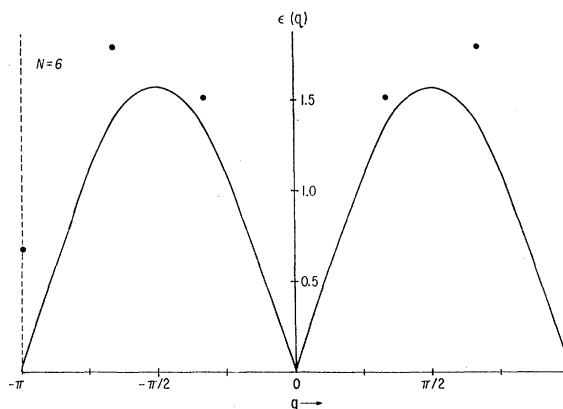


FIG. 1. Spin-wave spectrum for a chain of six atoms. The solid curve shows the spectrum for the infinite chain.

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¹ H. Bethe, *Z. Physik* **71**, 205 (1931) and in *Handbuch der Physik*, edited by S. Flügge (Springer Verlag, Berlin, 1933), Vol. XXIV/2, p. 604.

² L. Hulthén, *Arkiv Mat. Astron. Fysik* **26A**, 1 (1938).

³ L. F. Mattheiss, *Phys. Rev.* **123**, 1209 (1961).

⁴ For chains of 6, 8, and 10 atoms, R. Orbach computed all the energy levels [*Phys. Rev.* **115**, 1181 (1959)], but, unfortunately, not the corresponding k values, and consequently failed to obtain the correct spectrum.

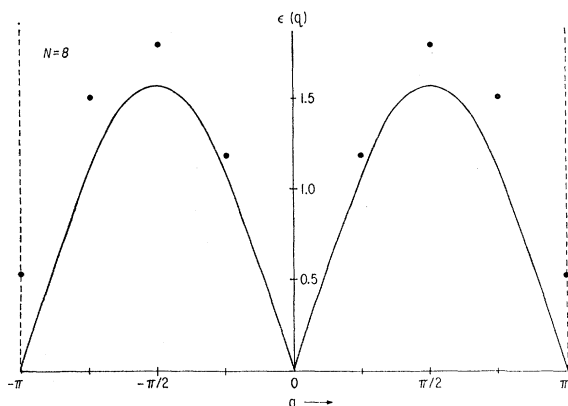


FIG. 2. Spin-wave spectrum for a chain of eight atoms. The solid curve shows the spectrum for the infinite chain.

introduced by Bethe is helpful for this purpose. It is possible to write all the eigenstates of the Heisenberg Hamiltonian in the following way:

$$\Psi = \sum a(n_1 \cdots n_r) \Phi(n_1 \cdots n_r), \quad (3)$$

where $\Phi(n_1 \cdots n_r)$ is obtained from the ferromagnetic ground state by reversing the spins at sites $n_1 \cdots n_r$ and Bethe assumed that the $a(n_1 \cdots n_r)$ for a state of spin $S = \frac{1}{2}N - j$ have the form

$$a(n_1 \cdots n_r) = \sum_{P_\mu} \sum_P \exp i \left(\sum_{j=1}^s k_{P_j} n_{\mu_j} + \frac{1}{2} \sum_{i < l} \varphi_{P_i, P_l} \right). \quad (4)$$

\sum_P indicates a summation over all the permutations of the numbers $k_1 \cdots k_s$ and \sum_{P_μ} a summation over all possible choices of s values n_μ from the set $n_1 \cdots n_r$. The k 's and the φ 's are solutions of the coupled equations

$$2 \cot(\varphi_{jl}/2) = \cot(k_j/2) - \cot(k_l/2), \quad -\pi \leq \varphi_{jl} \leq \pi. \quad (5)$$

$$Nk_j = 2\pi\lambda_j + \sum_l \varphi_{jl}, \quad (6)$$

where each λ_j is an integer. The energy of such a state is

$$E = - \sum_{j=1}^s (1 - \cos k_j), \quad (7)$$

and the corresponding wave number k is

$$k = \sum_j k_j = (2\pi/N) \sum_j \lambda_j. \quad (8)$$

The k_j 's and the φ_{jl} 's can be either real or complex. We shall restrict our considerations to the class C for which all the k_j 's and all the φ_{jl} 's are real, since a discussion by Bethe of the ordering of the energy levels suggests that the lowest energy state for a given k should belong to C . Each state of C is specified by a set of $s = \frac{1}{2}N - S$ integers λ_j satisfying the following conditions⁵:

$$0 < \lambda_j < N, \quad \lambda_j - \lambda_{j-1} > 1. \quad (9)$$

⁵ These conditions apply, in fact, only to the states with maximum projection of S on the z axis. The other degenerate states of the same spin are obtained by including additional λ 's all of which are zero.

In particular, the ground state, being a spin 0 state, corresponds to $\frac{1}{2}N$ integers λ_j which, according to the above rules, must be

$$1, 3, 5, \cdots (N-1). \quad (10)$$

The spin-wave states are to be sought among the spin 1 states with real k_j . Each of these states is defined by $(\frac{1}{2}N - 1)$ integers λ_j satisfying the above conditions. In this way $N(N+2)/8$ states can be obtained. We verified that for chains of 6 and 8 atoms these states do indeed include the spin-wave states which we found directly (Figs. 1 and 2). A calculation of this class of states for a chain of 16 atoms was performed on a Control Data 1604 computer. The energies ϵ of the lowest states are plotted as a function of q in Fig. 3.

IV. GENERAL PRESCRIPTION FOR SPIN-WAVE STATES (APPLICATION $N=48$)

The previous numerical calculations show that, for chains of 6, 8, and 16 atoms, the states of lowest energy and wave number q are given by the following choice of the λ_j :

$$\text{For } q > 0: 1, 3, 5, \cdots (N-2n-1), \\ (N-2n+2), \cdots (N-2), \quad (11)$$

$$\text{For } q < 0: 2, 4, 6, \cdots (2n-2), (2n+1), \cdots (N-1),$$

with $n = N|q|/2\pi$. For reasons of symmetry, the energy ϵ must be an even function of q . Assuming the above prescription for the choice of the λ_j to be valid in general, we computed numerically the spin-wave spectrum for a chain of 48 atoms. The results are plotted in Fig. 4. The results indicate fairly well the shape of the spectrum for a long chain. The spectrum has a periodicity of 2π due to the translational symmetry of the chain as expected, but also a nearly exact double periodicity of π . This behavior is surprisingly similar to that found in Anderson's two-sublattice spin-wave theory.⁶ Let us remark, however, that in Anderson's

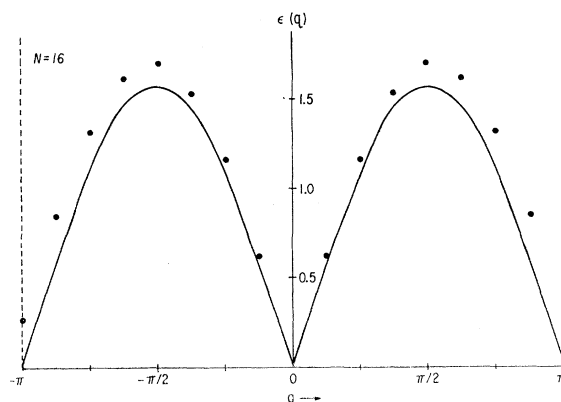


FIG. 3. Spin-wave spectrum for a chain of sixteen atoms. The solid curve shows the spectrum for the infinite chain.

⁶ P. W. Anderson, Phys. Rev. 86, 694 (1952).

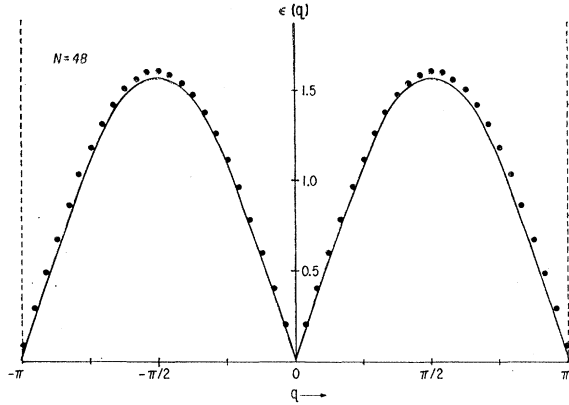


FIG. 4. Spin-wave spectrum for a chain of 48 atoms. The solid curve shows the spectrum for the infinite chain.

theory this double periodicity is artificially produced by doubling the basic translation and consequently halving the size of the Brillouin zone.

V. THE INFINITE CHAIN

In a manner analogous to the Hulthén calculation of the antiferromagnetic ground state it is possible also to calculate the spin-wave spectrum for an infinite chain. This is done by using the prescription of Sec. IV and by replacing discrete indices by continuous variables in Eqs. (4), (5), and (6). This process must be done carefully without leaving out terms of the order $1/N$ because, whereas the energy E_0 of the ground state is roughly proportional to N , the excitation energy which we want to calculate remains of the order of 1. For reasons of convenience, we compute the energy of a spin-wave state having $S_z=0$ and corresponding to a negative value of q . For this state, the sequence of the λ_j 's is

$$0, 2, 4, \dots (2n-2), (2n+1), \dots (N-1), \quad (12)$$

again with $n=N|q|/2\pi$.

Let the continuous variable x be defined by

$$x = (2j-1)/N, \quad 0 < x < 1 \quad \text{with } j=1, 2, \dots, N/2. \quad (13)$$

If we define functions $k(x)=k_j$, $\lambda(x)=\lambda_j/N$, and $\varphi(x,y)=\varphi_{ji}$, then Eqs. (4), (5), and (6) become

$$2 \cot \frac{\varphi(x,y)}{2} = \cot \frac{k(x)}{2} - \cot \frac{k(y)}{2}, \quad (14)$$

$$k(x) = 2\pi\lambda(x) + \frac{1}{2} \int_0^1 \varphi(x,y) dy, \quad (15)$$

$$E = -\frac{N}{2} \int_0^1 [1 - \cos k(x)] dx. \quad (16)$$

According to (12), $\lambda(x)$ is given by

$$\lambda(x) = (2j-2)/N = x - 1/N \quad \text{for } j \leq n \text{ or } x < |q|/\pi, \quad (17)$$

$$\lambda(x) = (2j-1)/N = x \quad \text{for } j > n \text{ or } x > |q|/\pi. \quad (18)$$

Therefore, we may write

$$\lambda(x) = x - (1/N)\Theta(|q|/\pi - x), \quad (19)$$

where $\Theta(x)$ is the step function. Let us remark that, according to (10), the function $\lambda_0(x)$ corresponding to the antiferromagnetic ground state would be

$$\lambda_0(x) = x. \quad (20)$$

Eliminating $\varphi(x,y)$ between Eqs. (14) and (15), we obtain

$$k(x) = 2\pi[x - (1/N)\Theta(|q|/\pi - x)] + \int_0^1 \arccot \cot \left\{ \frac{1}{2} \cot \left[\frac{k(x)}{2} \right] - \frac{1}{2} \cot \left[\frac{k(y)}{2} \right] \right\} dy, \quad (21)$$

with $-(\pi/2) \leq \arccot \cot k < (\pi/2)$. The differentiation of this equation with respect to k yields

$$1 = \pi \frac{dx}{dk} [1 + (2/N)\delta(x - |q|/\pi) + \{\sin[k(x)/2]\}^{-2} \times \int_0^1 \{4 + [\cot(k(x)/2) - \cot(k(y)/2)]^2\}^{-1} dy]. \quad (22)$$

Following Hulthén, we make the change of variable

$$\xi \equiv \cot[k(x)/2] \quad (23)$$

$$-dx/d\xi = f(\xi). \quad (24)$$

Letting ξ_0 be the value of ξ corresponding to $x = |q|/\pi$, we obtain

$$\delta(x - |q|/\pi) = \delta(\xi - \xi_0) |d\xi/dx| = \delta(\xi - \xi_0) [1/f(\xi)]. \quad (25)$$

After this transformation, the equation becomes

$$f(\xi) + (2/\pi) \int_{-\infty}^{+\infty} f(\eta) [4 + (\xi - \eta)^2]^{-1} d\eta = (2/\pi) (I + \xi^2)^{-1} - (2/N) \delta(\xi - \xi_0). \quad (26)$$

On the other hand, the energy is given by

$$E = -N \int_{-\infty}^{+\infty} f(\xi) [1 + \xi^2]^{-1} d\xi. \quad (27)$$

By using $\lambda_0(x)$ instead of $\lambda(x)$, we would obtain the Hulthén integral equation for the function $f(\xi)$ corresponding to the ground state. This equation can be derived from (26) by omitting the term in $(1/N)$. Equation (26) can now be solved easily. Putting

$$f(\xi) = f_0(\xi) + \Delta f(\xi) \quad (28)$$

we may write

$$\Delta f(\xi) = -(2/N) \int_{-\infty}^{+\infty} R(\xi, \eta) \delta(\eta - \xi_0) d\eta = -(2/N) R(\xi, \xi_0), \quad (29)$$

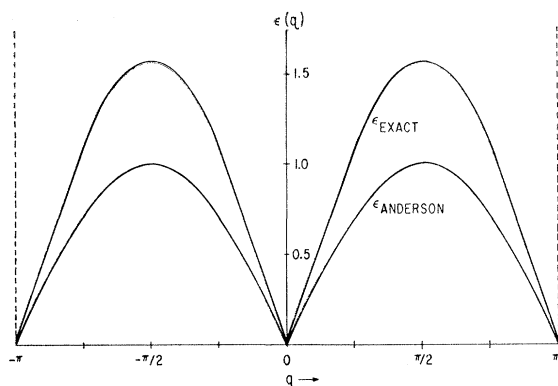


FIG. 5. The spin-wave spectrum in the exact case and in Anderson's approximation.

where $R(\xi, \eta)$ is the resolvent of Eq. (26) and has been calculated by Hulthén

$$R(\xi, \eta) = \delta(\xi - \eta) + \sum_{n=1}^{\infty} \frac{(-1)^n}{\pi} \frac{2n}{(2n^2) + (\xi - \eta)^2}. \quad (30)$$

Now putting

$$E = E_0 + \epsilon, \quad (31)$$

we deduce from (27), (29), and (30)

$$\begin{aligned} \epsilon &= -N \int_{-\infty}^{\infty} \Delta f(\xi) [1 + \xi^2]^{-1} d\xi \\ &= 2 \sum_{n=0}^{\infty} \frac{(-1)^n (2n+1)}{(2n+1)^2 + \xi_0^2} \\ &= \pi/2 \cosh(\tfrac{1}{2}\pi \xi_0). \end{aligned} \quad (32)$$

Now we must express ξ_0 as a function of q . To do this we recall the relation between x and ξ given by Eq. (23) and the following boundary conditions:

$$\begin{aligned} x=0 & \text{ for } \xi = -\infty, \\ x=1 & \text{ for } \xi = +\infty. \end{aligned} \quad (33)$$

This equation can be simplified by replacing $f(\xi)$ by $f_0(\xi)$, since the terms omitted are of order $1/N$ and may safely be neglected. As was shown by Hulthén,

$$f_0(\xi) = 1/2 \cosh(\tfrac{1}{2}\pi \xi), \quad (34)$$

and consequently Eq. (23) becomes

$$-dx/d\xi = 1/2 \cosh(\tfrac{1}{2}\pi \xi). \quad (35)$$

Integrating this equation and taking into account the boundary conditions we get

$$\sinh(\tfrac{1}{2}\pi \xi) = \cot(\pi x). \quad (36)$$

Remembering that ξ_0 is the value of ξ for which $x = |q|/\pi$, we obtain

$$\sinh(\tfrac{1}{2}\pi \xi_0) = \cot(|q|). \quad (37)$$

From this result and from Eq. (32) it follows that the spin-wave spectrum is given by

$$\begin{aligned} \epsilon &= \pi/2 \cosh(\tfrac{1}{2}\pi \xi_0) \\ &= \tfrac{1}{2}\pi |\sin q|. \end{aligned} \quad (38)$$

This result agrees very well with the spectra found directly for finite chains, and has been plotted on each figure. It is interesting to note that the double periodicity mentioned above is now exact. This fact facilitates comparison with the approximate expression obtained by Anderson, which automatically exhibits this double periodicity.

$$\epsilon_{\text{Anderson}} = |\sin q|. \quad (39)$$

Also, our spin-wave states, being spin 1 states, are threefold degenerate, whereas Anderson's spin-wave states have only two components. Anderson's approximation is really not valid for a linear chain and spin $\frac{1}{2}$, but it gives a surprisingly good value for the energy of the antiferromagnetic ground state ($E_{0 \text{ Anderson}} = -0.6817$; $E_{0 \text{ Exact}} = -0.6931$). Therefore, it is interesting to note the discrepancy between his spin-wave spectrum and the exact one. Both spectra are plotted in Fig. 5.

VI. SUMMARY AND CONCLUSION

For the sake of clarity it may be useful now to summarize the work of the preceding paragraphs. In Sec. II we have considered the case of short chains of 6 and 8 atoms. The energies and the quantum numbers (total spin S and wave number k) have been calculated. The ground state has spin 0 and wave number k_0 ($k_0 = 0$ if $N/2$ is even, $k_0 = \pi$ if $N/2$ is odd). For a given value of $k \neq k_0$, the states of lowest energy have spin 1 and therefore can be identified with spin-wave states. In Sec. III we introduce a class C of eigenstates originally presented by Bethe and Hulthén, and we observe that the states previously identified as spin-wave states for 6 and 8 atom chains are included in this class. On this basis we have assumed that for any value of N the spin-wave states belong to C . In accordance with this assumption we have calculated the states C of spin 1 for a 16 atom chain and from them selected as spin waves the states of lowest energy. In Sec. IV we have introduced a prescription for determining in advance which states in the class C are the spin-wave states. We have verified this prescription by comparison with the results obtained for the 6, 8, and 16 atom chains and have used it to calculate the spin-wave spectrum of a 48 atom chain. In Sec. V the same prescription has been used to obtain the spin-wave spectrum for an infinite chain and has been found to have the form $\epsilon = \tfrac{1}{2}\pi |\sin q|$ where $q = k - k_0$. This result differs from the approximate result of Anderson by the factor $\pi/2$.

Aside from questions of rigor, two points of interpretation remain unresolved. The first one concerns the real origin of the double periodicity mentioned above. As we have shown, this double periodicity is a feature of Anderson's two-sublattice theory. It appears, however, that it has nothing to do with long-range order, first because it is possible to find models without long-range order which display this double periodicity, and second because the ground state itself is probably not ordered. The second point concerns the number of spin-wave states. In the rigorous case, the spin-wave states, being eigenstates of spin 1, are triply degenerate

and correspond to values of k ranging from $-\pi$ to π . On the other hand, in a two-sublattice model, for each value of k , ranging from $-\pi/2$ to $\pi/2$, there are only two spin waves. It is not obvious how these two points of view can be reconciled.

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Optical Properties of Bound Exciton Complexes in Cadmium Sulfide

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The absorption and fluorescent spectra of "pure" CdS platelets (impurity concentrations $\sim 10^{17}/\text{cc}$) have been studied at low temperatures. In addition to intrinsic exciton lines, many sharp absorption and fluorescent lines were observed at slightly lower energies. Many of these lines are due to transitions involving bound excitons, in which the light creates (or destroys) an exciton bound to a neutral or charged donor or acceptor. Arguments from the known-band symmetries and electron g values permit the identification of the generic centers (neutral donor, neutral acceptor, charged center) with which particular transitions are associated. Transitions in which excitons from the second valence band are bound were also observed, in some cases lifetime broadened by phonon transitions to excitons from the first valence band. States due to neutral donors and neutral acceptors are usually both observed in the same crystal. This nonequilibrium situation is caused by the trapping of holes made by the light

which is being used to study the crystal. The "bleaching" of the trapped holes by the application of infrared light during ordinary transmission measurements near the band gap supports the generic transition assignments given. Centers of appropriate symmetries exhibit splittings due to electron-hole and hole-hole j - j coupling. The magnitudes of these splittings agree with crude theoretical estimates. The oscillator strength per center should be directly related to these splittings for the case of excitons bound to neutral impurities. Several different donors are discernible, but only a single acceptor is observed. The generic classification and energies of the observed centers should make possible the combined chemical and optical identification of the corresponding donors and acceptor in doped crystals. The arguments which permit the identification of the centers can easily be generalized to the case of cubic crystals.

I. INTRODUCTION

EXCITON states represent excited states of a pure crystal. When excitons are studied in real crystals, it is frequently found that many optical effects, such as absorption and fluorescence occur at photon energies less than the exciton energies, yet the character of these effects strongly suggest that they are connected with both excitons and crystals imperfections. Lampert¹ has suggested a variety of models for this type of center in which states are described as being analogous to H_2 , H_2^+ , and H^- . By observing the fluorescence at low temperatures from silicon crystals of known impurity content, Haynes² has identified centers, arising from

neutral donors and acceptors, which bear an analogy to H_2 . This paper describes a number of these "bound" (or "impurity") exciton states which occur in CdS.³ This material has a particularly simple band structure with band extrema at $k=0$ in the Brillouin zone, and the properties of the intrinsic excitons which arise from these extrema are well known.⁴ The CdS crystals which have been used for the present experiments and which, therefore, are of sufficiently good quality to give the sharp lines which will be described, are grown from the vapor without the intentional addition of impurities. The crystals do, however, have many imperfections present which are responsible for the bound exciton

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