orientations are irregularly distributed throughout the lattice and, furthermore, may change discontinuously from time to time. This model yields the correct contribution to c_v above the transition and, in virtue of the cooperative nature of the phenomenon, accounts qualitatively for the higher value of c_v, *viz.* 22 cal./mol-deg., below it.

In conclusion the writer desires to acknowledge his indebtedness to Professor Krefeld and Mr. Kenyon, of the Department of Civil Engineering at Columbia University, for their cooperation and assistance in preparing the specimens; to Mr. Richard Scheib, for his constant aid in the construction and manipulation of the apparatus; and to Dr. S. L. Quimby, who followed the progress of the research with helpful counsel and encouragement.

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Paramagnetic Relaxation Times for Titanium and Chrome Alum

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The relaxation times for spin-lattice coupling in titanium and chrome alum are computed on the basis of a specific model obtained by combining the thermodynamic theory of Casimir and du Pré with the writer's previous treatment of the normal modes of a cluster of the form $X \cdot 6H_2O$, where X contains an incomplete shell. The calculation includes both the first-order or direct processes important at low temperatures, and the second-order or "Raman" type of term predominant in the liquid-air region. There is no difficulty in understanding the observed absence of dispersion in titanium alum at liquid-air temperatures, but, barring crystal imperfections, it is hard to understand this absence at helium temperatures unless the nearest excited states are unreasonably deep. The agreement between the orders of magnitude of the calculated and experimental relaxation times is adequate in chromium both at high and low temperatures. The calculations predict, in agreement with experiments, that at liquid-air temperatures the relaxation time should increase when a constant field H_0 is applied and should be independent of the direction of H_0. The computed increase, however, is apparently not great enough. At helium temperatures, τ is theoretically not quite isotropic, and $d\tau/dH_0$ has the wrong sign, unless one abandons the usual formula $\rho_\omega \sim \omega^2$ for the density of lattice oscillators. The calculations on chromium should also apply qualitatively to iron alum, discussed at the very end.

I. Introduction

A NOTEWORTHY series of experiments on magnetic absorption and dispersion in paramagnetic media at radio and lower frequencies have been performed within the last few years by Gorter and other Dutch physicists.[1] In solid bodies the spin and orbit are largely decoupled, and the magnetism results almost entirely from spin. At first sight, it may seem that, owing to this decoupling, the spin moment is a constant of the motion, and so does not undergo any of the oscillations prerequisite to absorption or dispersion. The constancy is, however, spoiled by "spin-spin coupling," i.e., interaction between the spins of different paramagnetic atoms, and also by a slight potential energy of alignment of spin relative to the crystal lattice which arises because the spin is never perfectly decoupled from the orbit, and so indirectly feels the influence of the crystalline Stark effect acting on the orbit. The measurements on absorption and dispersion are particularly instructive because of the light which they shed on (*a*) the relaxation time τ_s involved in spin-spin interaction and (*b*) that τ characteristic of the coupling between spin and lattice. The present paper is devoted to τ rather than τ_s. Ordinarily τ_s is small compared to τ and is unimportant at the frequencies employed experimentally. The most elegant way of determining τ is furnished by the thermodynamic treatment of Casimir and du Pré,[2]

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[1] See *Physica*, from 1936 on, or the dissertations of Brons and of Teunissen (Groningen, 1939).

[2] H. B. G. Casimir and F. K. du Pré, Physica **5**, 507; also especially Casimir, Physica **6**, 156 (1939).

the essence of which is as follows: If the impressed frequency ω is small compared with $1/\tau_s$, the spins are in thermodynamic equilibrium with each other so that it makes sense to talk of a "spin temperature" T_s. The latter, however, will not be the same as the lattice temperature if ω is comparable with, or larger than $1/\tau$. Obviously the magnetic susceptibility will be of the isothermal variety in the region $\omega \ll 1/\tau$, where spin and lattice are in equilibrium, but becomes adiabatic when $\omega \gg 1/\tau$. The critical transition region $\omega \sim 1/\tau$ is characterized by dispersion (cf. our later Eq. (27)) and by determining this region, τ can be evaluated experimentally.

The theoretical calculation of τ was begun by Waller.[3] He assumed that the lattice vibrations influence the spin only by modulating the spin-spin interaction, and as a result obtained relaxation times entirely too large to agree with experiment. Actually the modulations of the crystalline Stark effect are more important. Even so, however, the attempts of Heitler, Teller,[4] and Fierz[5] to include schematically the latter type of modulation still lead to estimates too large by a factor about 10^2 to 10^4.

There are two types of relaxation effects which affect $1/\tau$, and the results of previous calculations on both these contributions to $1/\tau$ have always been too small, even when fairly liberal allowance has been made for possible ambiguities in uncertain factors. One type, the only variety important at low temperatures, is that in which the spin system absorbs a quantum of energy from the lattice vibrations, or else imparts a quantum to the latter. This we shall call the "direct process," as it is the analog of simple absorption or emission in radiation theory. The second type, predominant at high temperatures, is that where the spin absorbs a quantum of one frequency, and scatters that of another. This we shall allude to as the Raman process, for it is similar to incoherent scattering in optics.

A further puzzle has been the fact that titanium alum empirically exhibits much shorter relaxation times than the usual (i.e., ferric or chrome) alums. In fact, the relaxation time τ for the titanium alum is so short that no dispersion at all can be detected in the frequency range so far employed experimentally, so that one can say that $\tau \leqq 10^{-3}$ sec. and $\tau \leqq 10^{-7}$ sec. at helium and liquid-air temperatures, respectively. The corresponding value for the ordinary alums are of the order 10^{-2} and 10^{-6}. Now the ground level of titanium alum is only doubly degenerate, and so, in virtue of a well-known theorem of Kramers, cannot split in a crystalline field. Hence one might expect, at first sight, the lattice vibrations to be unable to modulate the crystalline Stark effect, and so not to influence the spin system except via the spin-spin interaction, which is too small. Thus one would anticipate that titanium should exhibit a very much longer, rather than shorter, relaxation time than the other alums.

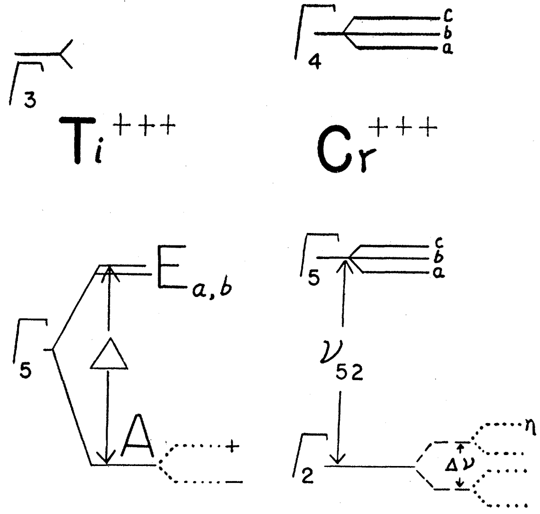

FIG. 1. Solid lines refer to orbital energy levels. States associated with the same Γ index coincide in a strictly cubic field. The dashed lines show the incomplete decomposition of the spin structure of the basic orbital level by a trigonal crystalline field, and the dotted lines illustrate the complete resolution by an applied magnetic field. The diagram is obviously not to scale, for the trigonal splitting Δ is small compared with a cubic interval such as ν_{52}, and the spin separations are very small compared with the orbital ones.

However, as Kronig[6] has already pointed out, and as we have also found independently, the idea that titanium cannot interact with the lattice via the Stark effect is based on a misconception. Matrix elements due to this interaction do appear. They have the property of being proportional to the frequency ω of the energy

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[3] I. Waller, Zeits. f. Physik **79**, 370 (1932).

[4] W. Heitler and E. Teller, Proc. Roy. Soc. **155**, 629 (1936).

[5] M. Fierz, Physica **5**, 433 (1938).

[6] R. de L. Kronig, Physica **6**, 33 (1939).

quantum exchanged between the spin and the lattice in the direct effect, and to the product of the incident and scattered frequencies in the Raman case. These elements are of the nonadiabatic nature, i.e., disappear in the limit $\omega = 0$, and so there is no contradiction of Kramers' theorem. On the other hand, our calculations in Sections VI and VII show that the most important terms in chromium or iron are of the adiabatic variety.

In the present paper we shall give explicit calculations of the paramagnetic relaxation times of titanium and chrome alum as typical of ions in which the important effects are, respectively, nonadiabatic and adiabatic. Generally speaking, the nonadiabatic terms are insignificant, but they are abnormally strong in Ti^{+++} because small frequency denominators are encountered in the perturbation calculation, because of the existence of low-lying excited levels. The latter are separated from the ground state in Ti^{+++} only in virtue of the small, noncubic portion of the crystalline field, rather than by a large cubic splitting as in Cr^{+++} (cf. Fig. 1).

The model which we use can be described as a combination of the thermodynamic theory of Casimir,[2] and the analysis which we made in a previous paper,[7] henceforth called l.c., of the Jahn-Teller effect in clusters of the form $X \cdot 6H_2O$. In the alums, the most important part of the crystalline potential exerted on the paramagnetic ion is doubtless that arising from the surrounding water molecules of coordination. So we are led to study the interaction between the magnetic moment of the paramagnetic ion and the normal vibrational coordinates (Fig. 2) of a complex $X \cdot 6H_2O$, as was done in the calculations of l.c. The latter were ostensibly in connection with the static paramagnetic susceptibility, but can be extended in a natural way to paramagnetic relaxation by expanding the normal coordinates in terms of the Debye elastic waves, as we shall do in Section II. As explained in l.c., the theory of the normal modes of vibration is quite different from the usual, standard classical variety when the complex contains a degenerate atom, as is the case with our paramagnetic ions with an odd number of electrons. Namely, a fundamental theorem of Jahn and Teller informs us that unless the degeneracy is lifted, the normal coordinates appear linearly rather than quadratically. It is only because of this linearity that the relaxation times are short enough to be important.

The calculations with a detailed model are of necessity somewhat long and involved, and cannot claim a high degree of accuracy, but still they do appear rather essential because purely schematic estimates, such as those of Heitler, Teller, Fierz, and Kronig are not at all reliable. Thus it proves that when the computations are made for chromium with an explicit model (Sections VI and VII) the calculated relaxation times are no longer larger than the observed values. On the other hand, the relaxation times yielded by our calculation for titanium at low temperatures (direct process, Section III) are larger by a factor 10^2, for a given separation Δ in Fig. 1, than the provisional estimate of Kronig. At liquid-air temperatures (Raman process, Section IV) our computed relaxation times are a great deal smaller than Kronig's for the same Δ, because his Raman matrix elements vanish in the limit $H = 0$, whereas ours do not. This difference arises because his model was too simplified to exhibit the most general type of term. We find that there is no difficulty in understanding the absence of observed disperion in titanium alum at liquid-air temperatures, even if Δ is as large as 10^3 cm^{-1}. Quite irrespective of the question of orders of magnitude, the calculations are of interest because they lead to certain general conclusions (Section VIII) regarding the dependence on the magnitude and direction of the applied magnetic field H_0 which do not depend on numerical values of the constants, and which furnish a rather interesting test of the thermodynamic model and the usual theory of lattice vibrations. Previous schematic estimates of the transition probability did not use the properties of the thermodynamic model explicitly enough to reveal the necessary relationships.

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[7] J. H. Van Vleck, J. Chem. Phys. **7**, 72 (1939); referred to henceforth as l.c. The following typographical errata in this paper may be noted: Eq. (24) read $-C_1(d^3\,{}^4F)$ and $-C_2(d^3\,{}^4F)$ in place of $-C_1(d^2\,{}^4F)$ and $-C_2(d^2\,{}^3F)$, respectively; Table II, read Q_4' in place of Q_3; Eq. (8), p. 64 of the article immediately preceding l.c., read $\cos 3(\beta_i - \beta_0)$ for $\cos (\beta_i - \beta_0)$.

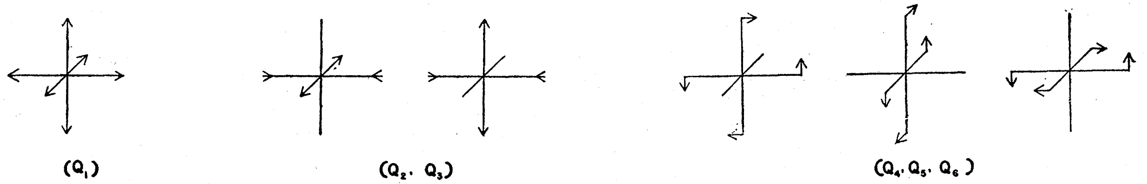

FIG. 2. Even modes of vibration of the complex Ti·6H$_2$O or Cr·6H$_2$O.

II. THE HAMILTONIAN FUNCTION FOR TITANIUM

Apart from modulations due to thermal vibrations, the crystalline field acting on a paramagnetic ion in the alums is of trigonal, but nearly cubic symmetry.[8] In titanium, unlike chromium, the calculation may be made by considering only those states which belong to the same orbital cubic representation Γ_5 as the ground level. Namely, nonvanishing elements of spin-orbit coupling are obtained by considering transitions merely internal to Γ_5, and so in comparison the effect of matrix elements nondiagonal in the cubic representation, which involve much higher frequencies, is unimportant. Thus only three orbital levels need to be considered, *viz.*, the nondegenerate ground state $\Gamma_5 A$, and the two components a,b of the doubly degenerate excited state $\Gamma_5 E$, as shown in Fig. 1. We henceforth omit the index Γ_5, since it is common to all states under consideration. Superposed there are two possibilities for spin orientation denoted by subscripts + and − when they need to be distinguished. The Hamiltonian function may be written

$$\mathcal{H}=\mathcal{H}_O+\mathcal{H}_L+\mathcal{H}_Z+\mathcal{H}_{SO}+\mathcal{H}_{OL}+\mathcal{H}_{SS}. \tag{1}$$

Here $\mathcal{H}_O$ is the "Stark" energy of the orbit, regarded as completely decoupled from the spin. It arises from the crystalline potential exerted by the surrounding atoms at their equilibrium positions. $\mathcal{H}_L$ is the "lattice" energy, due to thermal motions of the atoms, or in other words the Debye waves. These oscillations may, to a sufficient approximation for our purposes, be regarded as simple harmonic. In our system of representation, both $\mathcal{H}_O$ and $\mathcal{H}_L$ are diagonal. Their characteristic values are, with the most convenient choice of origin (zero energy for A), respectively,

$$\mathcal{H}_O(A)=0,\quad \mathcal{H}_O(E_a)=\mathcal{H}_O(E_b)=h\Delta,\quad \mathcal{H}_L=\sum_i h\omega_i(n_i+\tfrac{1}{2}), \tag{2}$$

where n_i is the number of quanta associated with the ith mode of vibration, of frequency ω_i.

The Zeeman energy $\mathcal{H}_Z$ plays a role in our calculations primarily in lifting the Kramers degeneracy. Without removal of the latter, there would be no energy to be exchanged with the lattice when the spin "turns over." We shall use a system of representation in which the spin is space quantized relative to the axis of the field H, which does not in general coincide with the trigonal axis. Then the part of $\mathcal{H}_Z$ due to spin is diagonal, and has the characteristic values

$$\mathcal{H}_Z(A_+)=\mathcal{H}_Z(E_+)=\beta H,\quad \mathcal{H}_Z(A_-)=\mathcal{H}_Z(E_-)=-\beta H.\quad (\beta=he/4\pi mc). \tag{3}$$

If there is no appreciable applied magnetic field, the Kramers degeneracy is lifted primarily by the spin-spin interaction

$$\mathcal{H}_{SS}=\sum_j V_{ij},\quad \text{with}\quad V_{ij}=4\beta^2\sum_i[\mathbf{S}_i\cdot\mathbf{S}_j-3r_{ij}^{-2}(\mathbf{S}_i\cdot\mathbf{r}_{ij})(\mathbf{S}_j\cdot\mathbf{r}_{ij})]r_{ij}^{-3}. \tag{4}$$

We shall neglect the modulation of the spin-spin energy by lattice vibrations. Although this modulation represents the type of spin-lattice coupling originally considered by Waller, it is now well recognized to be too small to be significant, and is much weaker than the spin-lattice interaction which we will obtain via the Stark effect. However, $\mathcal{H}_{SS}$ can still be of importance in lifting the Kramers degeneracy. For our purposes, as we will show more fully in Section VIII in connection with

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[8] See x-ray data by H. C. Lipson and C. A. Beevers, Proc. Roy. Soc. **148**, 664 (1935).

the Temperley effect, it is adequate to use Kronig and Bouwkamp's[9] approximation of regarding the spin-spin interaction as equivalent to a random magnetic field whose intensity is distributed according to the Gaussian law. We therefore henceforth drop $\mathcal{H}_{SS}$ from the Hamiltonian function, and interpret H in the Zeeman energy, not as merely the external magnetic field, but rather as the vector resultant of the applied field H_0, and the internal field due to spin-spin interaction. The applied static field H_0 is not to be confused with the much weaker, radiofrequency field which is used to measure the alternating susceptibility or dispersion.

The term $\mathcal{H}_{SO}$ in the Hamiltonian function is the spin-orbit energy $\zeta L\cdot S$. Its matrix elements are

$$\begin{gathered}\mathcal{H}_{SO}(E_{a\pm};E_{b\pm})=\pm\tfrac{1}{2}i\zeta l_{zz'},\quad \mathcal{H}_{SO}(A_\pm;E_{a\pm})=\pm\tfrac{1}{2}i\zeta l_{yz'},\quad \mathcal{H}_{SO}(A_\pm;E_{b\pm})=\pm\tfrac{1}{2}i\zeta l_{xz'},\\ \mathcal{H}_{SO}(E_{a\pm};E_{b\mp})=\tfrac{1}{2}i\zeta(l_{zx'}\pm il_{zy'}),\quad \mathcal{H}_{SO}(A_\pm;E_{a\mp})=\tfrac{1}{2}i\zeta(l_{yx'}\pm il_{yy'}),\\ \mathcal{H}_{SO}(A_\pm;E_{b\mp})=\tfrac{1}{2}i\zeta(l_{xx'}\pm il_{xy'}).\end{gathered}\tag{5}$$

Here the l's are the direction cosines connecting two sets of axes x,y,z and x',y',z' such that the trigonal axis is along z and H is along the z' axis. Only nonvanishing elements are written out. Elements in which all the initial and final indices are interchanged can be obtained from the Hermitian property. The result (5) can be obtained by noting that matrix elements of spin angular momentum are of the usual Pauli type referred to the x',y',z' axes, while those of the orbital angular momentum L can be obtained by using wave functions as given in Eqs. (20) and (21) of l.c. With proper orientation of the x,y axes one has $L_z(E_a;E_b)=L_y(A;E_a)=L_x(A;E_b)=i$. Corresponding to these matrix elements, there are also off-diagonal elements of the Zeeman energy which arise entirely from the orbital moment, and which have the values

$$\mathcal{H}_Z(E_{a\pm};E_{b\pm})=i\beta Hl_{zz'},\quad \mathcal{H}_z(A_\pm;E_{a\pm})=i\beta Hl_{yz'},\quad \mathcal{H}_z(A_\pm;E_{b\pm})=i\beta Hl_{xz'}.\tag{6}$$

The portion $\mathcal{H}_{OL}$ of (1) is that which gives the orbit-lattice coupling, and arises from modulation of the crystalline Stark effect by the elastic waves. The great bulk of the Stark splitting comes from the fields due to the nearby water molecules of coordination. The thermal vibrations cause these molecules to be instantaneously nearer or more remote from the paramagnetic cation than at their equilibrium positions, and so cause oscillations in the Stark pattern. Now the vibrations of a complex of the form $X\cdot 6H_2O$ are conveniently specified by a set of normal coordinates Q_1, Q_2, Q_3, Q_4, Q_5, Q_6 or Q_1, Q_2, Q_3, Q_4', Q_5', Q_6' described in detail in l.c. so that their definitions need not be repeated here. The quantities Q_4',Q_5',Q_6' are linear combinations of the vibrations Q_4,Q_5,Q_6 shown in Fig. 2. There are also other coordinates $Q_7,\cdots,Q_{21}$ but they appear only quadratically and so do not concern us. Because of the Jahn-Teller effect there are matrix elements of the crystalline potential linear in $Q_2,\cdots,Q_6$. These elements are found in Eq. (25) of l.c. to be

$$\begin{gathered}\mathcal{H}_{OL}(A_\pm;E_{a\pm})=\surd 6aQ_3+\tfrac{1}{3}\surd 3bQ_6',\quad \mathcal{H}_{OL}(A_\pm;E_{b\pm})=-\surd 6aQ_2+\tfrac{1}{3}\surd 3bQ_5',\\ \mathcal{H}_{OL}(E_{a\pm};E_{b\pm})=\surd 3aQ_2+\surd\tfrac{2}{3}bQ_5',\quad \mathcal{H}_{OL}(E_{a\pm};E_{a\pm})=\surd 3aQ_3-\surd\tfrac{2}{3}bQ_6'-\surd\tfrac{1}{3}bQ_4',\\ \mathcal{H}_{OL}(E_{b\pm};E_{b\pm})=-\surd 3aQ_3+\surd\tfrac{2}{3}bQ_6'-\surd\tfrac{1}{3}bQ_4',\quad H_{OL}(A_\pm;A_\pm)=2\surd\tfrac{1}{3}bQ_4'\end{gathered}\tag{7}$$

$$\text{with}\quad a=3\rho_1{}^0/7-25\rho_2{}^0/63,\quad b=-6\rho_1{}^0/7+10\rho_2{}^0/21,\quad \rho_1{}^0=-4e\mu\overline{r_0{}^2}R^{-5},\quad \rho_2{}^0=-6e\mu\overline{r_0{}^4}R^{-7}.\tag{8}$$

Here the bars over r^2 and r^4 denote, respectively, the mean square and mean fourth power radius of the electron orbit, and R denotes the equilibrium distance from the cation to any one of the six water molecules. The latter, in our model, each have a dipole moment μ which we suppose radially directed and which we regard as responsible for the crystalline field. The results of our calculation would not be significantly modified if a point charge instead of dipole field were used.

The Q's will continually oscillate due to the thermal motions of the lattice. They are thus in turn

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[9] R. de L. Kronig and C. J. Bouwkamp, Physica **5**, 521 (1938).

to be regarded as linear functions of the normal coordinates q_i associated with the lattice heat waves so that

$$Q_k = \sum_i a_{ki} q_i. \tag{9}$$

It is clearly to be understood that there are $3N$ coordinates q_i, where N is the number of atoms in the entire crystal, whereas there are only a small number of Q's, since the Q's are coordinates merely for the cluster $\mathrm{Ti}\cdot 6\mathrm{H_2O}$.

If the x_k, y_k, z_k be the Cartesian coordinates of a water molecule, with equilibrium values x_k^0, y_k^0, z_k^0 then x_k, for instance, depends on any given thermal mode i of vibration in the form

$$x_k - x_k^0 = q_i \Phi_{xi} \cos(\gamma_{ki} - \delta_i), \quad \gamma_{ki} = 2\pi\omega(\lambda_{xi} x_k^0 + \lambda_{yi} y_k^0 + \lambda_{zi} z_k^0)/v_i. \tag{10}$$

Here q_i and Φ_{xi}, Φ_{yi}, Φ_{zi} are the direction cosines of the amplitude of the wave q_i while v_i and λ_{xi}, λ_{yi}, λ_{zi} are its velocity, and the cosines specifying its direction of polarization. We shall suppose that the wave-length of the lattice vibration is large compared with the cluster's cross section $2R$ so that we can take

$$\cos(\gamma_{ki} - \delta_i) = \cos \delta_i + \gamma_{ki} \sin \delta_i. \tag{11}$$

This approximation is amply warranted in the calculations at helium temperatures, where the "direct process" is important. On the other hand, it must be kept in mind that at higher (i.e., liquid air) temperatures, where the Raman mechanism comes in, the most important frequencies are those near the high frequency "cut-off," of the Debye spectrum. These have wave-lengths of the order 10^{-7} cm, so that γ_{ki} is of the order unity ($2\pi R$ is about 1.2×10^{-7} cm). Using (10) (11), and the formulas of l.c. expressing the normal coordinates Q_k in terms of the x,y,z, we find that the coefficients a_{ki} in (9) have the following values

$$\begin{aligned} a_{2i} &= U(\lambda_{xi}\Phi_{xi} - \lambda_{yi}\Phi_{yi}), \quad a_{3i} = U(\lambda_{xi}\Phi_{xi} + \lambda_{yi}\Phi_{yi} - 2\lambda_{zi}\Phi_{zi})/\sqrt{3}, \\ a_{4i}' &= U(\lambda_{xi}\Phi_{yi} + \lambda_{yi}\Phi_{xi} + \lambda_{zi}\Phi_{xi} + \lambda_{xi}\Phi_{zi} + \lambda_{yi}\Phi_{zi} + \lambda_{zi}\Phi_{yi})/\sqrt{3}, \\ a_{5i}' &= U(\lambda_{xi}\Phi_{zi} + \lambda_{zi}\Phi_{xi} - \lambda_{yi}\Phi_{zi} - \lambda_{zi}\Phi_{yi})/\sqrt{2}, \\ a_{6i}' &= U(\lambda_{xi}\Phi_{zi} + \lambda_{zi}\Phi_{xi} + \lambda_{yi}\Phi_{zi} + \lambda_{zi}\Phi_{yi} - 2\lambda_{yi}\Phi_{xi} - 2\lambda_{xi}\Phi_{yi})/\sqrt{6}, \end{aligned} \tag{12}$$

with

$$U = (2\pi R\omega_i/v_i)\sin\delta_i. \tag{13}$$

The matrix elements of the lattice coordinates q_i are given by the harmonic oscillator expression

$$q_i(n_i; n_i+1) = q_i(n_i+1; n_i) = [h(n_i+1)/4\pi^2 M\omega_i]^{\frac{1}{2}}, \tag{14}$$

where M is the total mass of the crystal, due, of course, largely to atoms other than titanium. This formula contains a factor 4 rather than the customary 8 in the denominator, because not all the atoms of the crystal are located at antinodes, and so do not share in the full amplitude of vibration.

It must be cautioned that (14) is not a particularly good approximation, perhaps the weakest link in our whole calculation. It assumes that the amplitude of vibration is the same for all varieties of atoms in the crystal, regardless of their mass, whereas actually the heavy atoms have smaller, the lighter larger, motions than average.

III. CALCULATION OF DIRECT PROCESSES FOR TITANIUM

We now make a perturbation calculation, regarding the crystalline Stark potential, the lattice vibrations, and the spin part of the Zeeman energy as incorporated in the original Hamiltonian function, and the spin-orbit and orbit-lattice couplings as together constituting the perturbation. When the calculation is carried out to the second order, it turns out that the new or transformed Hamiltonian function will contain elements of the desired type $\mathcal{H}(A \pm n_i; A \mp n_i + 1)$ in which the spin "turns over" and the lattice vibration simultaneously changes by one quantum unit. The appropriate perturbation formula[10] is

$$\mathcal{H}_{\text{new}}(ii') = \sum_k [\mathcal{H}(ik)\mathcal{H}(ki')/h\nu(ik)]. \tag{15}$$

The frequency denominators in (15), represent, as usual, the change in the diagonal part of the energy, which is the sum of (1), (2), and (3). The conservation of energy, requires that $W(i) = W(i')$. One of the $\mathcal{H}$ factors in the right side of (15) is to be taken as coming from $\mathcal{H}_{OL}$, and the other from $\mathcal{H}_{SO}$, since clearly it is only by superposition of spin-orbit and orbit-lattice coupling that we will obtain the desired final spin-lattice coupling. There are two types of terms, in which $\mathcal{H}_{OL}$ and $\mathcal{H}_{SO}$ are, respectively, the first and second $\mathcal{H}$ factors, and vice versa. These two types of terms very nearly cancel because by (5) and the Hermitian property any element of $\mathcal{H}_{SO}$ changes sign when one makes the interchange of initial and final indices involved in reversing the order of $\mathcal{H}_{SO}$ and $\mathcal{H}_{OL}$. A corresponding sign change does not occur in $\mathcal{H}_{OL}$. The compensation of terms due to the two possible orderings would be complete were it not that the Zeeman energy makes the energy of the appropriate intermediate state slightly different in the two cases. Obviously Kramers' theorem requires complete compensation unless $H \neq 0$. Thus

$$\begin{aligned}\mathcal{H}_{\text{new}}(A_+n_i;A_-n_i+1) &= \sum_{\alpha=a,\,b}\left\{\frac{\mathcal{H}_{SO}(A_+;E_{\alpha-})\mathcal{H}_{OL}(E_\alpha n_i;An_i+1)}{-h(\Delta-2H\beta)}+\frac{\mathcal{H}_{OL}(An_i;E_\alpha n_i+1)\mathcal{H}_{SO}(E_{\alpha+};A_-)}{-h(\Delta+2H\beta)}\right\}\\ &= -4\beta Hh^{-1}\Delta^{-1}\sum_{a=\alpha,\,\beta}\mathcal{H}_{SO}(A_+;E_{\alpha-})\mathcal{H}_{OL}(E_\alpha n_i;An_i+1).\end{aligned} \tag{16}$$

Here we have made use of the fact that $2\beta H$ can be regarded as very small compared with the Stark splitting Δ, and that the conservation of energy demands that the change $h\omega$ in lattice energy just counterbalance that $2\beta H$ in Zeeman energy.

Equations (15) and (16), as we have used them, do not allow for the effect of the orbital Zeeman energy (6). Actually, the latter leads to terms coordinate in importance with (16). These terms are to be computed by adding to (15) the expression

$$\mathcal{H}_{\text{new}}(ii') = \sum_{j,\,k}[\mathcal{H}(ij)\mathcal{H}(jk)\mathcal{H}(ki')/h\nu(ij)h\nu(ik)], \tag{17}$$

where one $\mathcal{H}$ factor is to be taken from the spin-orbit energy (5), another from the orbit-lattice coupling (7), and the remaining factor from the interaction energy (6) of the orbital moment with the magnetic field H. Formula (17) can give results coordinate in order of magnitude with (15) because in (17) nonvanishing contributions can be obtained without considering the modulation of the frequency denominators by the magnetic field or the lattice vibrations.

By standard perturbation theory, the probability that an atom in the state A_+ reverse its spin and pass to A_-, exciting a quantum of vibration to the lattice is

$$A_{+\rightarrow-} = (4\pi^2/h^2)\langle\rho_\omega\,|\,\mathcal{H}_{\text{new}}(A_+n_i;A_-n_i+1)\,|^2\rangle_{\text{Av}}. \tag{18}$$

Here the average is over all directions of propagation and polarization of the oscillators, as well as over all values of the quantum number n_i. The expression ρ_ω is the oscillator density relative to frequency, and is to be evaluated at $\omega = 2\beta H$. By a well-known formula, the values of ρ_ω for longitudinal and transverse waves are, respectively,

$$\rho_{\omega l} = 4\pi\omega^2 V/v_l^3, \quad \rho_{\omega t} = 8\pi\omega^2 V/v_t^3, \tag{19}$$

where v_l and v_t are, respectively, the velocities for longitudinal and transverse waves, while V is the volume of the crystal. We have now to compute the explicit value of (16) by means of (5–14),

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[10] Cf., for instance, W. Heitler, *The Quantum Theory of Radiation*, p. 90, Eq. (43b).

and perform the averaging in (18). In connection with the latter, we utilize the fact that

$$\langle n_i\rangle_{\mathrm{Av}}=1/(1-e^{-h\omega/kT}), \tag{20}$$

$$\begin{aligned}&\langle\lambda_{qi}{}^2\Phi_{qi}{}^2\rangle_{\mathrm{Av}}=1/5,\quad \langle\lambda_{qi}{}^2\Phi_{pi}{}^2\rangle_{\mathrm{Av}}=\langle\lambda_{qi}\Phi_{qi}\lambda_{pi}\Phi_{pi}\rangle_{\mathrm{Av}}=1/15 \text{ (longitudinal waves)}\\ &\langle\lambda_{qi}{}^2\Phi_{qi}{}^2\rangle_{\mathrm{Av}}=1/15,\quad \langle\lambda_{qi}\Phi_{qi}\lambda_{pi}\Phi_{pi}\rangle_{\mathrm{Av}}=-1/30,\quad \langle\lambda_{qi}{}^2\Phi_{pi}{}^2\rangle_{\mathrm{Av}}=2/15 \text{ (transverse)}(p,q=x,y,z;\, p\neq q).\end{aligned} \tag{21}$$

Averages of products analogous to the above, but involving three different subscripts, are zero. The work of averaging is considerably shortened by noting that the average of cross product terms in the normal coordinates, such as Q_2Q_3, is zero; this follows from the orthogonality of our normal coordinates, as well as from explicit computation by (12). Hence the relaxations due to the different normal modes of vibration of the surrounding water cluster can be regarded as taking place independently. For every given wave there is also another wave which stands in a reciprocal relation as regards the position of nodes and antinodes. Thus, the effective mean value of $\sin^2\delta_l$ is $\frac{1}{2}$. In consequence of this fact and of (21), one finds that the average squares of the coefficients (12) are

$$\langle a_{2i}{}^2\rangle_{\mathrm{Av}}=\cdots=\langle a_{6i}'^2\rangle_{\mathrm{Av}}=(8\pi^2R^2\omega_i{}^2/15v_l{}^2)(\text{longitudinal}),\quad =(6\pi^2R^2\omega_i{}^2/15v_t{}^2)(\text{transverse}). \tag{22}$$

It is also necessary to average over the four possible directions for the trigonal axis, related to each other as are the four body-diagonals of a cube, for in the alums there are these four different types of surroundings for a paramagnetic ion, so that all told there is cubic macroscopic symmetry.[8] Because of the latter, we may equate to $\frac{1}{3}$ the square of any direction cosine, while cross-products such as $\lambda_{xi}\lambda_{yi}$ etc. drop out. Were only the spin portion (3) of the Zeeman energy retained, only these easily averaged quadratic forms would be encountered, but when the orbital part (6) is included, the expression for the transition probability involves biquadratic expressions in the direction cosines, for which the averaging is somewhat more complicated. We finally find

$$A_{+\rightarrow-}=(1+\epsilon_1+5\epsilon_2w)\beta H^5Be^{h\omega/kT}/(e^{h\omega/kT}-1),\quad (\omega=2\beta H) \tag{23}$$

with

$$B=\frac{2}{3}\left(\frac{16\pi^3V}{hM}\right)\frac{R^2\zeta^2}{h^4\Delta^4}\left[\frac{8}{5}a^2+\frac{4}{45}b^2\right]2^5h^{-3}\beta^4\left[\frac{1}{v_l{}^5}+\frac{3}{2v_t{}^5}\right], \tag{24}$$

$$\begin{gathered}w=m_1{}^2m_2{}^2+m_1{}^2m_3{}^2+m_2{}^2m_3{}^2,\quad \epsilon_1=(144a^2+56b^2)/(864a^2+48b^2),\\ 5\epsilon_2=(252a^2-10b^2)/(864a^2+48b^2).\end{gathered} \tag{25}$$

Here m_1,m_2,m_3 denote the direction cosines of the magnetic field relative to the principal cubic axes of the alum, and consequently the ϵ_2 term gives a dependence of the relaxation on the direction of the applied field. If the orbital Zeeman energy (6) were omitted, the expressions ϵ_1,ϵ_2 would be zero.

It is customary to say that $A_{+\rightarrow-}$ is of the order of the relaxation time due to transfer of energy between spin and lattice. However, the very beautiful thermodynamic treatment of Casimir and du Pré[2] gives us a more exact view of things. They assume that the spin system has a temperature T_S which is not the same as that T of the lattice. The specific heat C_H of the spin portion at constant applied field H_0, is of the form[2]

$$C_H=[b'+C'H_0{}^2]/T_S{}^2\quad\text{with}\quad C'=4N\beta^2\cdot\tfrac{1}{3}S(S+1). \tag{26}$$

It is supposed that the spin specific heat is very small compared with that of the container, an assumption warranted at helium temperatures only if the specimen is in contact with a constant temperature bath, for the specific heat of the lattice proper is very small at low temperatures because of the Debye T^3 law. Fortunately such contact appears to be present in the usual experiments. The heat flow from spin to lattice is taken to be $\alpha(T_S-T)$, in other words proportional to the difference between the spin and lattice temperatures. Casimir and du Pré[2] show that the relation between the static susceptibility χ_0 and that χ_ν appropriate to a frequency ν is

$$\chi_\nu=\chi_0(1-F)+[\chi_0F/(1+4\pi^2\tau^2\nu^2)],\quad \text{with}\quad \tau=C_H/\alpha,\quad F=C'H_0^2/(b'+C'H_0^2). \tag{27}$$

The relaxation time τ is thus the ratio of the spin specific heat C_H to the conductivity constant α governing the heat flow between spin and lattice.

The rate of transfer of heat from the spin to the lattice is

$$dQ/dt=2\beta H[N_{\frac{1}{2}}A_{+\rightarrow-}-N_{-\frac{1}{2}}A_{-\rightarrow+}], \tag{28}$$

where N_{M_S} is the number of atoms with spatial spin quantum number M_S. The relation connecting N_{M_S} with the spin temperature T_S is

$$N_{M_S}=Ne^{-2\beta HM_S/kT_S}/[e^{2\beta HS/kT_S}+\cdots+e^{-2\beta HS/kT_S}]\sim Ne^{-2\beta HM_S/kT_S}/(2S+1), \tag{29}$$

where for present purposes we can put $S=\frac{1}{2}$, but we give (29) in a general form so that it can later be used in chromium.

The expression for $A_{-\rightarrow+}$ is identical with that (23) for $A_{+\rightarrow-}$, except that the factor $e^{h\omega/kT}$ is missing from the numerator, to allow for the fact that the Boltzmann factor is different for an upper than for a lower state of a lattice oscillator. Since $\beta H/kT=\frac{1}{2}h\omega/kT$ is small, we may replace the denominator of (20) by $2\beta H/kT$, and we see that

$$\alpha=\lim_{T_S\rightarrow T}[(T_S-T)^{-1}dQ/dt]=(1+\epsilon_1+5\epsilon_2w)BNH^6\beta^2/T. \tag{30}$$

The final expression must be averaged with respect to the field H, which is the resultant of the applied field H_0 and the apparent field due to spin-spin interaction. The latter we suppose distributed according to the Gaussian law, so that the probability for instance, that the x component of H falls in the interval H, $H+dH$ is $(6/\pi K^2)^{\frac{1}{2}}\exp[-3(H_x-H_{0x})^2/2K^2]dH$. Here K denotes the mean square resultant spin-spin field, inclusive of x,y, and z components. By appropriate adaptation of the formulas of Kronig and Bouwkamp,[9] one finds that[11]

$$K^2=2g^2\beta^2S(S+1)\textstyle\sum_j r_{ij}^{-6}=[4\beta^2S(S+1)][28.8/r_0^6], \tag{31}$$

where $r_0=2^{1/6}N^{-1/3}$ is the distance between titanium atoms which are nearest neighbors. The same expression can also be obtained in somewhat more quantum-mechanical fashion by using matrix algebra, along lines given by Waller.[3] The numerical value of K given by (31) for titanium alum is 130 gauss.

The term b' in the specific heat (26) is in the case of titanium due entirely to the spin-spin interaction, and can be computed accurately.[12] Its value is $b'=\frac{1}{2}NK^2\beta^2$. As we might conjecture, the resulting formula for C_H is the same as that which would be obtained by setting $b'=0$, and replacing H_0^2 by $H_0^2+\frac{1}{2}K^2$ in (26), i.e., by taking the effective square of the field as the sum of the true square of the applied field H_0 and half the mean square spin-spin field. The factor $\frac{1}{2}$ arises in connection with the latter because spin-spin interaction represents mutual energy.

When one utilizes (26) and (30), and performs the Gaussian averaging explained above, one finds that the formula for the relaxation time $\tau=C_H/\alpha$ becomes[13]

$$\tau=\frac{H_0^2+\frac{1}{2}K^2}{kTB[(1+\epsilon_1+5\epsilon_2w_0)H_0^6+\frac{1}{3}(21+21\epsilon_1+10\epsilon_2+55\epsilon_2w_0)H_0^4K^2+(35/3)(1+\epsilon_1+\epsilon_2)H_0^2K^4+(35/9)(1+\epsilon_1+\epsilon_2)K^6]} \tag{32}$$

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[11] Our value of K^2 is, however, larger by a factor $3(S+1)/S$ than the corresponding mean square field of Kronig and Bouwkamp, reference 9, since one should use the quantal rather than classical square of the moment, and since we are dealing with the sum of the squares of the x, y, and z components.

[12] I. Waller, Zeits. f. Physik **104**, 132 (1936); J. H. Van Vleck, J. Chem. Physics **5**, 320 (1937); M. H. Hebb and E. M. Purcell, *ibid.* **5**, 338 (1937).

[13] If $K=0$, one can show that the expression τ given by (32), (or later by Eq. (43) for the Raman process) satisfies the relation $1/\tau=2\langle A_{+\rightarrow-}\rangle_{\text{Av}}$ proposed by Gorter and Kronig (Physica **3**, 1009 (1936)). With $K\neq0$, however, the proportionality factor ceases to be 2. This fact is not surprising, as with $K\neq0$, the spins interact with each other, and their postulate that equilibrium is secured solely by contact with a thermostat (lattice) no longer applies.

where w_0 is similar to the expression w defined in (25) except that the direction cosines now relate to the applied field H_0 rather than to the total effective field H. Usually measurements are made on a powder, and then w_0 can obviously be replaced by its mean value $\frac{1}{5}$. The values of ϵ_1, ϵ_2 are, respectively, 0.66 and 0.01, so that the correction for the orbital Zeeman effect, represented by the ϵ_1, ϵ_2 terms makes τ about three-fifths as large as it would be otherwise. Since ϵ_2 is so small, the anisotropy coming from the w_0 terms is negligible even for a single crystal, amounting to only about one percent and with existing experimental accuracy τ should be independent of direction.

To evaluate (8), (24), and (32) numerically we use the following values of the constants

$$\begin{gathered} R=2\times10^{-8}\ \text{cm}^{-1}, \quad \rho_1{}^0R=14{,}400\ \text{cm}^{-1}, \quad \rho_2{}^0R=10{,}800\ \text{cm}^{-1}, \\ M/V=2.0, \quad \Delta=1000\ \text{cm}^{-1}, \quad \zeta=154\ \text{cm}^{-1}, \quad v_t=v_l=2.3\times10^5\ \text{cm/sec.} \end{gathered} \tag{33}$$

The values of R and M/V (the density) are furnished directly by the crystalline dimensions, while ζ is known from spectroscopy. The above determinations of $\rho_1{}^0$, $\rho_2{}^0$ and Δ, based partly on empirical Stark splittings and partly on an explicit model treating the field from the water molecules as of dipole character, are fully explained in l.c.[7] or elsewhere.[14] Our calculations are not so refined that it is worth while to try and distinguish between the longitudinal and transverse velocities of sound. Instead we shall use an affective common velocity $v=2.3\times10^5$ cm/sec., which is that given by specific heat data[15] when the effect of the two types of waves is not resolved. Actually the longitudinal velocity may be almost double the transverse one, but the error is not as serious as it would seem, since both in specific heats and in our relaxation calculations by far the greater weight is attached to the transverse waves, so that the effective common velocity is nearly the same as v_t. This is true not merely because the transverse vibrations are twice as numerous as the longitudinal, but also because the transverse velocity is lower and weighted according to a fairly high inverse power. Namely the specific heat formulas involve the inverse cube of v, while our expression (23–4) for the transition probability contains the inverse fifth power. (The inverse tenth occurs in our corresponding later formula (38) for Raman processes.) The lumping together of the two varieties of sound velocities would not be an adequate approximation if the longitudinal vibrations were appreciably more effective in modulating the Stark effect than are transverse disturbances of the same velocity and amplitude. Our explicit calculations indicate that fortunately this is not the case; contrary to Heitler and Teller's conjecture[4] that only the longitudinal waves would be important.

The values of τ computed from (32) with the aid of (33) are, 5×10^4, 1.7×10^2, and 1.8×10^{-2} sec., respectively, for applied fields H_0 of intensity 0, 10^3, and 10^4 gauss at a temperature T of 1.2 degrees. The agreement with experiment is miserable. The absence of any observed dispersion in the Leiden experiments[16] on titanium alum at helium temperatures shows that τ cannot possibly exceed 10^{-3} sec. for a range of field strengths about 100 to 2000 gauss. Our estimate of the relaxation time in fields of 1000 gauss is greater than Kronig's by a factor 10^4. Out of the 10^4, about 10^2 is due to his use of an interval Δ one-third of ours, while the remaining 10^2 is due to his estimating the matrix elements of $\mathcal{H}$ by rough considerations of orders of magnitude rather than with a model.

It appears impossible to eliminate the tremendous discrepancy between our results and the experimental data unless (*a*) the frequency distribution law (19) for the lattice waves is grossly in

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[14] The value of Δ was calculated, in a paper immediately preceding l.c. (J. Chem. Phys. **7**, 61 (1939)) and was found to be 1450 cm^{-1}. This preceding article was unfortunately marred by an error, because its Eq. (14) did not include the contribution of the off-diagonal elements (47) of the present article to the splitting $\Delta\nu$ of the basic state of chromium. Further modification results from the fact that according to the recent measurements of Bleaney, reference 18, the splitting $\Delta\nu$ has the value 0.17 cm^{-1} in place of the primitive estimate 0.12 of Hebb and Purcell previously employed. When both corrections are taken into account, it is found that the amount of distortion of the water octohedron necessary to explain the observed $\Delta\nu$ is about a quarter as great as previously calculated and the calculated splittings for vanadium and titanium become, respectively, 545 and 1075 cm^{-1}. At best only qualitative significance should be attached to this calculation, so we use the round value $\Delta=1000$ cm^{-1}. The revised estimate for vanadium raises difficulties, as it is questionable whether the trigonal symmetry of the deepest state of the cluster $V\cdot6H_2O$ is sufficiently stabilized.

[15] Casimir, de Haas and de Klerk, Physica **6**, 241 (1939).

[16] W. J. de Haas and F. K. du Pré, Physica **5**, 969 (1938).

error or, (*b*) the Stark splitting is considerably smaller than the value 10^3 cm^{-1} assumed in (33). The possibility of (*a*) will be discussed in Section VIII. As regards (*b*), since Δ enters in the inverse fourth power in (24), our estimates of τ would be lowered by a factor 10^{-4} if the assumed value of Δ were reduced by a factor 10 to 100 cm^{-1}. Such a drastic change in Δ presents difficulties. Some calculations by the writer[14] indicate that it is very difficult to find a reasonable crystalline potential which will reconcile a Δ of only 100 or 200 cm^{-1} in titanium with the splitting of 700 cm^{-1} in vanadium alum demanded by Siegert's theory of the magnetic behavior of V^{+++}, or with the behavior of the energy levels of Cr^{+++} indicated by adiabatic demagnetization data.

It should be mentioned that the reliability of the existing Leiden data, for titanium alum, is perhaps not beyond question, since, I am told, the crystals may have lost some of their water of hydration. The dehydration is doubtless insufficient to lower the density anything like enough to make exchange forces important, but, as mentioned to the writer by Dr. van den Handel, might warp the crystal so that it no longer has the ideal structure assumed in our calculation. The distortion could scarcely materially lower the interval Δ for all atoms, but fluctuations in the field due to the imperfection might cause an appreciable number of atoms to have values of Δ nearly zero, and so a large coupling to the lattice, as well as deviations from Curie's law could be obtained. This explanation seems rather fantastic, but further experimental work will be awaited with interest, especially since at present different specimens yield somewhat divergent results.

If the interval Δ is reduced to 100 cm^{-1}, or so, as appears necessary if the existing relaxation measurements are correct and the discrepancy is to be blamed on Δ, then the Raman terms become more important than the direct processes even at helium temperatures. We therefore proceed to examine the Raman mechanism. We shall see that it accounts nicely for the experimental results at liquid-air temperatures even if Δ is not reduced below 10^3 cm^{-1}.

IV. CALCULATION OF RAMAN PROCESSES FOR TITANIUM

In order to obtain transitions in which one lattice quantum is absorbed, and another emitted, we must compute the new Hamiltonian function by means of (17), taking two of the $\mathcal{H}$ factors in (17) to represent orbit-lattice coupling (7), and the other of the spin-orbit type (5). The frequency denominators ν are to be considered as representing the combined change in the orbital Stark energy levels and in the lattice vibrational energy. In the present computation, unlike that for the direct processes, the spin-spin and Zeeman contributions to the frequency ν may be disregarded. Consequently the absorbed and emitted vibrational quanta, which are in general very much larger than these contributions, may be taken to have a common value $h\omega$. In this respect our calculations differ materially from Kronig's. The appropriate elements of his transformed Hamiltonian function $\mathcal{H}_{\text{new}}$ vanish in the limit $H=0$. As a result, his calculated Raman transition probabilities turn out several orders smaller than ours, instead of larger as for the the direct processes. Written out explicitly, (17) becomes, in the present case,

$$\mathcal{H}_{\text{new}}(A_+n_in_j;A_-n_i-1n_j+1)=\left[\frac{f_{ij}^+-f_{ji}^-}{(-\Delta)(-\Delta+\omega)}+\frac{f_{ji}^--f_{ij}^+}{(-\Delta)(-\Delta-\omega)}+\frac{2g_{ij}^+-2g_{ji}^-}{-\Delta\omega}\right]$$
$$+\left[\frac{-g_{ij}^++g_{ji}^-}{(-\Delta+\omega)(+\omega)}+\frac{-g_{ji}^-+g_{ij}^+}{(-\Delta-\omega)(-\omega)}+\frac{h_{ij}^+}{(-\Delta+\omega)^2}+\frac{h_{ji}^-}{(-\Delta-\omega)^2}\right], \qquad (34)$$

with

$$f_{ij}^\pm=h^{-2}\textstyle\sum_{\alpha,\,\alpha'=a,\,b}\mathcal{H}_{SO}(A_+;E_{\alpha-})\mathcal{H}_{OL}(E_\alpha n_i;E_{\alpha'}n_i\mp1)\mathcal{H}_{OL}(E_{\alpha'}n_j;An_j\pm1),$$
$$g_{ij}^\pm=h^{-2}\textstyle\sum_{\alpha=a,\,b}\mathcal{H}_{SO}(A_+;E_{\alpha-})\mathcal{H}_{OL}(E_\alpha n_i;An_i\mp1)\mathcal{H}_{OL}(An_j;An_j\pm1), \qquad (35)$$
$$h_{ij}^+=-h_{ji}^-=h^{-2}\textstyle\sum_{\alpha,\,\alpha'=a,\,b}\mathcal{H}_{OL}(An_i;E_\alpha n_i\mp1)\mathcal{H}_{SO}(E_{\alpha+};E_{\alpha'-})\mathcal{H}_{OL}(E_{\alpha'}n_j;An_j+1).$$

The various terms on the right side of (34) represent the different possible orders of the three $\mathcal{H}$

factors on the right side of (17). The first bracket of (34) represents the contribution of terms in which $\mathcal{H}_{SO}$ is the first or last factor, while the second bracket comes from the terms in which $\mathcal{H}_{SO}$ is the middle factor. In writing (35), we have made use of the fact that by (6) or (13) the matrix elements of $\mathcal{H}_{OL}$ are invariant under interchange of the initial and final orbital indices, or of the initial and final vibrational indices (i.e., $\mathcal{H}_{OL}(An_i;En_i')=\mathcal{H}(En_i;An_i')=\mathcal{H}(An_i';En_i)$), while by (5) and the Hermetian property, the elements of $\mathcal{H}_{SO}$ alter their sign when the initial and final orbital indices are permuted. The various terms of (34) do not quite destroy each other when $\omega\neq 0$. We may suppose ω small compared with Δ, and so (34) becomes

$$\mathcal{H}_{\text{new}}(A_+n_in_j;A_-n_i-1n_j+1)=\omega\Delta^{-3}[2f_{ij}^+-2f_{ji}^-+2g_{ij}^+-2g_{ji}^-+4h_{ij}^+]. \tag{36}$$

The transition probability $A_{+\rightarrow -}$ that an atom reverse the sign of its spin is

$$A_{+\rightarrow -}=(4\pi^2/h^2)\int_0^{\theta k/h}\langle[|\mathcal{H}_{\text{new}}(A_+n_in_j;A_-n_i-1n_j+1)|^2\rho_{\omega_i}\rho_{\omega_j}\rangle_{\text{Av}}d\omega_i. \tag{37}$$

Here θ is the usual Debye characteristic temperature, and $\omega_i=\omega_j$, but we cannot set $\rho_{\omega_i}=\rho_{\omega_j}$ because i may be a transverse wave, and j a transverse one, or vice versa, so that different oscillator densities (19) may be relevant. As compared with (18) there is the difference that we must integrate over all oscillator frequencies, since the conservation of energy is secured by the equality of the absorbed and emitted quanta, and so the available oscillators are no longer restricted to those of very low frequency in the Zeeman range.

The average in (37) is, of course, over all amounts of excitation and of directions of propagation and of polarization for the two oscillators now involved. The spatial averaging for them may be done independently. The requisite formulas are the same as those given in (20) and (22) and discussed thereafter. On computing the explicit value of (37) by means of (5–11), and on performing the requisite averaging, it is finally found, after considerable straight forward calculation, that

$$A_{+\rightarrow -}=64(256V^2\zeta^2R^4\pi^4h^2/75\Delta^6M^2)(v_l^{-5}+\tfrac{3}{2}v_t^{-5})^2[a^4+(11/18)a^2b^2+(11/648)b^4]I_8, \tag{38}$$

where

$$I_n=\int_0^{\theta k/h}[\omega^n e^{+h\omega/kT}/(e^{h\omega/kT}-1)^2]d\omega \tag{39}$$

with $n=8$ for present purposes. The integral I_8 represents the appropriate statistical factor for the two oscillators participating in our Raman process, one of which is excited and the other de-excited. The expression (19) for the oscillator density would suggest that ω should occur to only the fourth power; however, the eighth power enters when one allows for the appearance of ω in (13), (14), (36), etc. At low temperatures, where $T/\theta\ll 1$, as in the helium range, one can legitimately make the approximation

$$I_n=\int_0^{\infty}\omega^n e^{-h\omega/kT}d\omega=n!(kT/h)^{n+1}. \tag{40}$$

At higher temperatures, where $T\sim\theta$, as in the liquid-air region, the great bulk of the integral (39) comes from the vicinity of the cut-off frequency $\omega_0=h\theta/k$, so that without great error, we can expand the exponential factors in (39) as a Taylor's series about ω_0, and keep only the constant, and perhaps also the linear term. Then (39) becomes

$$I_n=\left(\frac{k\theta}{h}\right)^{n+1}\left[\frac{e^{\theta/T}}{(n+1)(e^{\theta/T}-1)^2}+\frac{\theta}{(n+1)(n+2)T}\,\frac{(e^{\theta/T}+1)e^{\theta/T}}{(e^{\theta/T}-1)^3}-\cdots\right]. \tag{41}$$

When $n=8$, the limiting value of (39) appropriate to the case $\theta/T\ll 1$ is clearly $k^9h^{-9}\theta^7T^2/7$. A corresponding limiting formula is also yielded by (41), except that the denominator becomes 9 instead of 7 if only the first term of (41) is utilized, and $7\frac{1}{2}$ if both members of (41) are included. The expression (41) is an adequate approximation for our purposes unless θ/T is large, but the experiments are never conducted at such high temperatures that it is allowable to use the limiting values proportional to T^2 characteristic of $\theta/T \ll 1$. Formula (41) tends to underestimate the value of I_n but this is proably a good thing, as it tends to counterbalance the error latent at higher temperatures in the approximation (11), wherein the wave-length was taken to be large compared with the interatomic distance.

To compute the relaxation time by the thermodynamic method, we note that the expression for the rate of transfer of energy to the lattice is still given by (28) with $N_{\frac{1}{2}}$, $N_{-\frac{1}{2}}$, as in (29). The transition probability $A_{-\rightarrow+}$ differs from $A_{+\rightarrow-}$ by a factor $e^{-2\beta H/kT}$, nearly, but not quite equal to unity. Up till now we regarded the absorbed and emitted quanta as equal, but this is not strictly true—otherwise no energy exchange would be possible. Instead the two quanta will differ by an amount $2\beta H$, where H is the resultant of the applied and spin-spin fields. In place of (30) and (32) we now have

$$\alpha = 2\beta^2 N(A_{+\rightarrow-}/kT^2)\langle H^2\rangle_{\text{Av}} = 2\beta^2 N(A_{+\rightarrow-}/kT^2)(H_0^2+K^2) \tag{42}$$

and

$$\tau = C_H/\alpha = \tfrac{1}{2}[(H_0^2+\tfrac{1}{2}K^2)/A_{+\rightarrow-}(H_0^2+K^2)]. \tag{43}$$

To evaluate τ at liquid-air temperatures, we need to know θ. We shall take $\theta = 90°$, as this is the magnitude yielded by the conventional formula $\theta = (vh/k)(3N/4\pi V)^{\frac{1}{3}}$, with $v = 2.3\times10^5$ cm/sec. With the values (33) of the other constants, one finds from (38), (41) and (43) that $\tau = 0.13\times10^{-8}$ sec. at 77°K if $H_0 \gg K$, and $\tau = 0.07\times10^{-8}$ if $H_0 \ll K$. Thus even if the interval Δ is kept as high as 10^3 cm^{-1}, the theory is adequate to explain the unusually short relaxation times characteristic of titanium alum at liquid-air temperatures. Namely, all that is known experimentally[17] is that from the absence of any observed dispersion over the frequency interval employed, τ must be less than 4×10^{-8} sec. at 77°K.

At helium temperatures, on the other hand, a relaxation time sufficiently small to agree with experiment can be obtained only if Δ is of the order 100 cm^{-1}, or if drastic changes be made instead in some of the other constants. Namely, if we use the constants (33) as they stand, and if $H_0 \gg K$, then by (38), (40), and (43), the value of τ at low temperatures is $1.0\times10^3/T^9$, at least 100,000 times too large. It is, however, possible to bring τ down to within the necessary limit $\tau < 10^{-3}$ sec., if we take $\Delta = 10^2$ cm^{-1}, as then τ becomes 0.2×10^{-3} at 1.2°K and 0.5×10^{-4} at 1.4°K.

If Δ is reduced sufficiently to bring agreement with experiment in the helium region, then the Raman mechanism is likely to be more important than the direct process even here. Namely, in fields of 1000 gauss, the value of τ for the direct process was found to be 1.7×10^{-2} sec. at 1.2°K with $\Delta = 10^2$ cm. This is about ten times as large a value of τ as our Raman estimate given above. At fields of the order 10^4 gauss or so, the direct process does, however, yield much the greater transition probability or smaller τ, because the direct interaction varies as the fourth power of H.

In the preceding paragraph we compared the Raman and direct processes on the assumption that agreement with experiment is to be obtained by altering Δ. If, on the other hand, the discrepancy is to be removed by altering other constants, i.e., increasing aR or bB, or assuming that the effective mass to be used in (14) is less than that of an average molecule, then it can be shown that the margin of superiority in favor of the Raman terms becomes even greater. However, if the distribution law (19) for the lattice oscillators is badly in error at low frequencies, a possibility which we discuss near the end of the paper, the direct process might be adequate to explain the absence of observed dispersion at helium temperatures. Another possibility is that some other mechanism than the lattice vibrations serves as the thermostat.

It would obviously be of interest if critical experiments could be performed which would decide between the direct and Raman mechanisms for temperatures in the helium range. Further evidence

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[17] Gorter, Teunissen and Dijkstra, Physica 5, 1013 (1938).

could be secured by studying the effect of diluting titanium with nonmagnetic ingredients in weak applied fields. (Some field is necessary, as F in Eq. (27) vanishes if $H_0=0$.) Dilution decreases the effective spin-spin field K, which enters quite differently in (43) and (32). With the Raman process, the relaxation time is slightly increased by dilution, but with the direct type it is materially lengthened so that ultimately a measurable dispersion should set in even without extending the measured frequencies to higher values than those employed in the existing Leiden experiments. It appears probable that in any case the beginning of the dispersion is not very far on the high frequency side of the present limit. Once the dispersion can be detected, an enormous difference between the two types of mechanisms will appear, for with Raman transitions, τ is tremendously temperature sensitive ($\sim T^{-9}$ if $T \ll \theta$) and increases slightly when a field is applied, whereas with the direct transfers τ varies but slightly with temperature, and is greatly diminished by introducing a field H_0.

Owing to the T^9 factor in the Raman mechanism, the equilibrium at the very low temperatures ($\sim$0.01 to 0.1°K) obtained by adiabatic demagnetization is undoubtedly achieved by the direct type of process. Despite the rather large values of the direct τ which we compute, Casimir[2] shows that the equilibrium takes place practically instantaneously in demagnetization experiments because of the fact that the lattice is no longer in a constant temperature bath, as in relaxation measurements such as we are discussing. Instead it is isolated from external contacts and hence has a very low heat capacity, proportional to T^3.

V. The Hamiltonian Function for Chromium

We now proceed to the corresponding calculations of the direct and Raman processes for chromium. As compared with titanium, there is the big difference (cf. Fig. 1) that the excited states belong to a different cubic representation than the ground level, so that it is necessary to consider matrix elements of the spin-orbit and orbit-lattice interaction which are nondiagonal in the cubic index Γ, and to specify the orbital states by their cubic representation. By extending somewhat the calculations of l.c., one finds the matrix elements of the spin-orbit interaction are

$$\mathcal{H}_{SO}(\Gamma_i\sigma_1;\Gamma_j\sigma_2)=\zeta\sum_{q=x,\,y,\,z}L_q(\Gamma_i;\Gamma_j)S_q(\sigma_1;\sigma_2), \tag{44}$$

with

$$\begin{aligned} L_z(\Gamma_2;\Gamma_{5a})&=L_x(\Gamma_2;\Gamma_{5b})=L_y(\Gamma_2;\Gamma_{5c})=+2i;\\ -L_y(\Gamma_{4a};\Gamma_{4b})&=L_x(\Gamma_{4a};\Gamma_{4c})=-L_z(\Gamma_{4b};\Gamma_{4c})=-\tfrac{3}{2}i;\\ L_y(\Gamma_{5a};\Gamma_{5b})&=-L_x(\Gamma_{5a};\Gamma_{5c})=+L_z(\Gamma_{5b};\Gamma_{5c})=-\tfrac{1}{2}i;\\ -L_y(\Gamma_{4a};\Gamma_{5b})&=-L_x(\Gamma_{4a};\Gamma_{5c})=-L_z(\Gamma_{4b};\Gamma_{5c})=L_y(\Gamma_{5a};\Gamma_{4b})=L_x(\Gamma_{5a};\Gamma_{4c})=L_z(\Gamma_{5b};\Gamma_{4c})=-\tfrac{1}{2}\sqrt{15}i, \end{aligned} \tag{45}$$

$$S_z(\sigma;\sigma)=\sigma,\quad (S_x+iS_y)(\sigma;\sigma-1)=[S(S+1)-\sigma(\sigma-1)]^{\frac{1}{2}},\quad (S=\tfrac{3}{2}). \tag{46}$$

The matrix elements of L are Hermitian, i.e., change sign on permutation of initial and final indices. The S matrices are also Hermitian and are, of course, the usual angular momentum matrices. Elements not written down (or obtained by mere interchange of initial and final indices) are all zero. The index σ gives the component of spin parallel to the z axis, which we choose as the axis of spin quantization. The x,y,z axes are taken as the principal cubic axes. We thus use a different choice of axes and of spin quantization than in the preceding section. It is not necessary to use a trigonal index (A or E) in connection with designating the orbital states, as the trigonal splitting of the upper state has no appreciable repercussion on the relaxation behavior of the ground state, since the latter is separated from excited states by a large interval due to the cubic part of the field. The three sub-states a,b,c of Γ_4 or Γ_5 are the same as the system of representation used in Eq. (21) of l.c. and are not eigenstates of the trigonal field.

The nonvanishing matrix elements of orbit-lattice coupling connecting the ground state Γ_2 with excited levels are

$$\mathcal{H}_{OL}(\Gamma_2 n_i;\Gamma_{4x}n_i\pm 1)=+Q_{4,6,5}(n_i;n_i\pm 1)[44\rho_1-5\rho_2]/11\sqrt{15},\quad (x=a,b,c) \tag{47}$$

where the subscripts 4,6,5 apply, respectively, to the cases a,b,c and where $\rho_1=-3\rho_1^0/7$, $\rho_2=+11\rho_2^0/7$, with ρ_1^0, ρ_2^0 defined as in (8). The only other matrix elements of $\mathcal{H}_{OL}$ needed in connection with the calculation of the direct process are those internal to Γ_5 i.e., of the form $\mathcal{H}_{OL}(\Gamma_{5x}n_3;\Gamma_{5y}n_3\pm 1)$. These are given in Eqs. (21) and (22d) of l.c.,[7] with a,b,c referring to the rows or columns of (21), and need not be repeated here. There are no matrix elements of $\mathcal{H}_{OL}$ connecting Γ_2 and Γ_5, or of the type Q_2, Q_3 joining Γ_2 and Γ_4. (This statement is easily proved from group theory, since the representations corresponding to Q_2, Q_3 and to Q_4, Q_5, Q_6 are, respectively, Γ_3 and Γ_5, and the appropriate direct products are $\Gamma_2\times\Gamma_5=\Gamma_4$, $\Gamma_2\times\Gamma_3=\Gamma_1+\Gamma_2+\Gamma_3$.) On the other hand, the orbital angular momentum involved in the spin-orbit coupling has the transformation properties of Γ_4, and so this interaction does not join Γ_2 and Γ_4. Such vanishing of the matrix elements materially simplifies the calculations.

VI. CALCULATION OF DIRECT PROCESSES FOR CHROMIUM

To compute the elements of the new or transformed Hamiltonian function to be used in (18), we employ the third-order expression (17), taking two of the $\mathcal{H}$ factors as due to the spin-orbit interaction, and one as due to orbit-lattice. The frequency denominators in (17) can be taken as the Stark splitting due to the cubic field alone, without the necessity of including the modulations due to either the lattice oscillations or the magnetic field. In this respect the present calculations differ materially from those on titanium. The reason is that we are now dealing with an atom whose basic state is a quartet. Its initial degeneracy is fourfold rather than twofold and so can be partially lifted without introducing magnetic fields even when the lattice vibrations are treated in an adiabatic fashion. Hence it is not necessary to allow for the modulation of the frequency denominators, which is a nonadiabatic effect. It is, however, essential to include two powers of the spin-orbit interaction rather than one as in the case of titanium, since the second-order expression (15) vanishes if we take one $\mathcal{H}$ factor as the spin-orbit, and the other as the orbit-lattice interaction. This vanishing of (15) is caused by the compensation of terms representing different orders of the factors, and would be spoiled if we allowed for modulation of the frequency denominators. In fact, such modulation was the cause of the direct relaxation effect in titanium. However, the corresponding effect in the present case of chromium is negligible. Namely, it is reduced in the ratio $\Delta^4/\nu_{52}{}^4$ as compared with titanium, inasmuch as the normal states is separated from excited levels by a large cubic splitting ν_{52} rather than by a comparatively small trigonal separation Δ.

Proceeding as above, we find that the matrix internal to Γ_2 in the new Hamiltonian function is

$$\mathcal{H}_{\text{new}}=\epsilon_1[Q_3(2S_z{}^2-S_x{}^2-S_y{}^2)+\sqrt{3}Q_2(S_y{}^2-S_x{}^2)]+\epsilon_2[Q_4(S_xS_y+S_yS_x)+Q_5(S_xS_z+S_zS_x)$$
$$+Q_6(S_yS_z+S_zS_y)]=\textstyle\sum_{k=2,\ldots,6}H_{\text{new}}{}^{(k)}Q_k \qquad (48)$$

with

$$\begin{aligned}\epsilon_1&=4\zeta^2[175\rho_2/396][h\nu_{52}]^{-2}\sqrt{3},\\ \epsilon_2&=4\zeta^2[\rho_1+(5\rho_2/33)][h\nu_{52}]^{-2}+8\zeta^2[\rho_1-(5\rho_2/44)][h\nu_{52}h\nu_{42}]^{-1}.\end{aligned} \qquad (49)$$

Here and elsewhere we use the abbreviation $h\nu_{52}=W(\Gamma_5)-W(\Gamma_2)$, etc. In (48), the S's are to be construed as matrices, whose elements are given by (46).

We can assume that the cubic potential is of fourth-order character $D'[x^4+y^4+z^4]$. This supposition involves no loss of generality since we are dealing with d electrons (cf. reference 14). Then the frequency denominators involved in (49) are

$$h\nu_{52}=10Dq,\quad h\nu_{42}=18Dq\quad\text{with}\quad Dq=2D'\overline{r^4}/105. \qquad (50)$$

Here Dq is the constant of Schlapp and Penney, which we shall take as having the value 1500 cm^{-1} (cf. p. 81 of l.c.[7]).

Let us imagine the matrix elements of the spin in (49) computed not in the system of representation (46), but rather in one which diagonalizes the combined energy, apart from fluctuations caused by lattice oscillations, of the spin in the magnetic field H, and in the electric field due to surrounding ions, which indirectly affects the spin via the spin-orbit coupling. Let the eigenstates of the energy, shown by dotted lines in Fig. 1, be denoted by $W_{\eta'}$, $W_{\eta''}$, $\cdots$. Then by obvious generalization of (25), (26) to systems with more than two spin components, the rate of transfer from spin to lattice, is

$$dQ/dt=\sum_{\eta',\eta''}N_{\eta'}A_{\eta'\rightarrow\eta''}(W_{\eta'}-W_{\eta''}). \tag{51}$$

The transition probabilities $A_{\eta'\rightarrow\eta''}$ are connected with the matrix elements in the η system of representation by relations analogous to (18), and the matrix elements of the Q's are, of course, still given by (9), (12), (14). One now has, however, $h\omega=W_{\eta''}-W_{\eta'}$ instead of $h\omega=2\beta H$, and $N_\eta=\frac{1}{4}Ne^{-W_\eta/kT_S}$ in place of (29). Since $A_{\eta'\rightarrow\eta''}=e^{h\omega/kT}A_{\eta''\rightarrow\eta'}$, and since we still have $h\omega/kT\ll1$, $T_S-T\ll T$ we can write

$$N_{\eta'}A_{\eta'\rightarrow\eta''}(W_{\eta'}-W_{\eta''})+N_{\eta''}A_{\eta''\rightarrow\eta'}(W_{\eta''}-W_{\eta'})=\tfrac{1}{8}N[A_{\eta'\rightarrow\eta''}+A_{\eta''\rightarrow\eta'}](W_{\eta'}-W_{\eta''})^2(T_S-T)/kT^2. \tag{52}$$

When average values are computed by means of (20) and (22), which reduces to $\langle n_i\rangle_{\text{Av}}=kT/h\omega$, it is found that $dQ/dt=\alpha(T_S-T)$ with

$$\alpha=NC\sum_{k=2\cdots6}\sum_{\eta',\eta''}|H^{(k)}(\eta';\eta'')|^2|W_{\eta'}-W_{\eta''}|^4,\quad C=R^2(4v_l^{-5}+6v_t^{-5})\pi^3V/15TMh^4. \tag{53}$$

Eq. (53) can also be written as

$$\alpha=NC\sum_{k=2,\ldots,6}\text{spur}\,[V_kW-WV_k]^2,\quad V_k=WH^{(k)}-H^{(k)}W, \tag{54}$$

where W is the matrix (internal to Γ_2) associated with the Hamiltonian function whose proper values are the W_η. The great advantage of writing (54) as a spur is that (54) is valid in any system of representation, and so it is not necessary to actually find the system which diagonalizes W. In chrome alum the matrix W has the structure

$$W=2\beta[H_xS_x+H_yS_y+H_zS_z]+\tfrac{1}{6}h\Delta\nu[S_x+S_y+S_z]^2. \tag{55}$$

The first member of (55) is clearly the Zeeman energy in the field H. The second is the energy of the crystalline electric field. The latter has trigonal rather than perfect cubic symmetry and so splits the quartet ${}^4\Gamma_2$ into two doublets, whose separation is denoted by $h\Delta\nu$, and which correspond, respectively, to $S_{z'}=\pm\frac{3}{2}$, and $S_{z'}=\pm\frac{1}{2}$, where the z' direction is parallel to the trigonal axis. The Hamiltonian function associated with the crystalline Stark effect may thus, apart from an additive constant, trivial for our purposes, be written as $S_{z'}{}^2h\Delta\nu/[(\frac{3}{2})^2-(\frac{1}{2})^2]$. The form employed in (55) follows from the fact that the trigonal axis is a body diagonal $x=y=z$ of our x,y,z system, so that $S_z'=[S_x+S_y+S_z]/\sqrt{3}$. The explicit value of the expression (54) for α can now be computed with the aid of (48) and (55), and the conventional commutation relations for angular momentum matrices. After some calculation, one finds that

$$\begin{aligned}\alpha=72C(2\beta)^4[(8\epsilon_1{}^2+3\epsilon_2{}^2)(H_x{}^4+H_y{}^4+H_z{}^4)+(10\epsilon_1{}^2+8\epsilon_2{}^2)(H_x{}^2H_y{}^2+H_y{}^2H_z{}^2+H_z{}^2H_x{}^2)]\\+C\beta^2h^2\Delta\nu^2(H_x{}^2+H_y{}^2+H_z{}^2)(3072\epsilon_1{}^2+1280\epsilon_2{}^2)+12Ch^4\Delta\nu^4(6\epsilon_1{}^2+2\epsilon_2{}^2).\end{aligned} \tag{56}$$

As in the calculations on titanium, we consider the magnetic field H to arise in part from an applied field H_0, and in part from an effective field H_s representing spin-spin interaction. As previously, we regard H_s to be oriented at random, and distributed in Gaussian fashion, with a root mean square value K. With these assumptions, and the corresponding averaging over H_s, Eq. (56) becomes

$$\begin{aligned}\alpha=\alpha'+72C(2\beta)^4[(8\epsilon_1{}^2+3\epsilon_2{}^2)(2H_0{}^2K^2+K^4)+(10\epsilon_1{}^2+8\epsilon_2{}^2)(\tfrac{2}{3}H_0{}^2K^2+\tfrac{1}{3}K^4)]\\+C\beta^2h^2\Delta\nu^2[3072\epsilon_1{}^2+1280\epsilon_2{}^2]K^2,\end{aligned} \tag{57}$$

where α' denotes the expression (56) with H everywhere replaced by H_0. On calculating the explicit value of the specific heat (26), for the present case of chromium, it is found that the relaxation time τ appearing in (27) becomes

$$\tau = C_H/\alpha = [\tfrac{1}{4}(h^2\Delta\nu^2) + 5(H_0{}^2 + \tfrac{1}{2}K^2)\beta^2]/\alpha T^2. \tag{58}$$

To compute numerical values, we recall that by definition $\rho_1 = -3\rho_1{}^0/7$, $\rho_2 = 11\rho_1{}^0/7$ and take $\rho_1{}^0$, $\rho_2{}^0$, v as in (33), but K and ζ are now, respectively, 290 gauss and 88 cm^{-1}. The density M/V is now 1.7 instead of 2.0, as we are dealing with $KCr(SO_4)_2 \cdot 12H_2O$ rather than $CsTi(SO_4)_2 \cdot 12H_2O$. The appropriate values of ν_{ij} are cited in connection with (50). The splitting $\Delta\nu$ we consider to be 0.17 cm^{-1}, as this is the value indicated by recent experiments on adiabatic demagnetization.[18] The computed values of τ at 1.4°K are then 0.011, 0.0090, 0.0067 and 0.0030 second, respectively, for $H_0 = 0$, 500, 1000, and 3000 gauss. Most of the energy transfer when $H_0 = 0$ results in virtue of the Stark splitting $\Delta\nu$ rather than the spin-spin coupling K, for if we take $K = 0$, the value of τ at $H_0 = 0$ is raised merely to 0.014 second.

The agreement with experiment as to order of magnitude is adequate. The only available experimental measurements are those made at Leiden, not yet in final form. A preliminary analysis of them, kindly communicated to the writer by Professor Casimir, yields relaxation times τ equal to 0.018 and 0.007 second at temperatures of 2° and 3.5°K, respectively, both at a field strength of 1350 gauss. The corresponding values yielded for these conditions by our calculations are 0.0035 and 0.0020 second. The experimental accuracy is estimated as only 20 percent, but the error in our calculations is doubtless even greater. It is gratifying that the calculated relaxation times actually turn out smaller than the observed values, inasmuch as in previous work there has been a pronounced discrepancy in the opposite direction.

However, the predicted dependence on field strength is entirely wrong, for theoretically the relaxation time should decrease when the field is increased, whereas experimentally the reverse is true. (The empirical increase of τ with H_0 is rather small, and conceivably the data might be consistent with a τ independent of ν, but even so the theoretical prediction $d\tau/dH_0 < 0$ is contradicted.) Possible explanations of this discrepancy will be sought for in Section VIII. The dependence on temperature is also incorrect. Theoretically τ should be proportional to $1/T$, whereas comparison of the data at 2° and 3.5°K indicates that more nearly $\tau \sim T^{-\frac{3}{2}}$ or T^{-2}.

VII. Calculation of Raman Processes for Chromium

We now proceed to the calculation of second-order processes for chromium. The mechanism for these is different than in the case of titanium. There are contributions from two main types of terms, I and II which prove to be approximately coordinate in importance and which are as follows:

I. Those which are obtained by using a fourth-order perturbation formula, analogous, except for order, to (15) or (17). Two of the $\mathcal{H}$ factors in the numerator are to be taken as due to spin-orbit interaction (44), and two due to orbit-lattice coupling.

II. Terms which are obtained by employing the third-order perturbation formula (17), but expanding the crystalline potential to the second rather than first order in the normal coordinates $Q_1, Q_2, \cdots$. The orbit-lattice coupling energy such as (47), or Eq. (21) of l.c., is then replaced by an expression of the second order in the Q's. In (17), one of the $\mathcal{H}$ factors is due to this extension of the orbit-lattice interaction, while the two others are contributed by the spin-orbit energy (44).

Besides I and II, there are two other types of contribution III, IV, as follows, which require examination, but which prove to be of minor importance.

III. Terms which result from the third-order formula (17), taking two of the $\mathcal{H}$ factors as due to the orbit-lattice energy (47), linear in the Q's, and one factor only as due to the spin-orbit energy, but allowing for the modulation of the frequency denominators by the energy changes in the lattice oscillators. In I and II, these denominators can be

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[18] B. Bleaney, in press.

regarded as arising from the cubic crystalline potential alone, but without the modulation, the structure III would make no contribution to the relaxation.

IV. Terms obtained by using the second-order formula (15), but expanding the orbit-lattice energy to the second order in the Q's as in II, and simultaneously allowing for the modulation of the frequency denominators as in III. One of the $\mathcal{H}$ factors is due to the second-order extension of the orbit-lattice interaction, and the other to the spin-orbit energy.

Effects I and II may be characterized as obtained by an adiabatic, and III–IV by a nonadiabatic perturbation calculation, since the modulation of the frequency denominators is essentially an allowance for the fact that the oscillations in the crystalline potential do not take place infinitely slowly. In making the calculation, one must be careful to notice that I and II contribute additively only to the transformed Hamiltonian function $\mathcal{H}_{\text{new}}$ and not to the transition probability, or to the heat transfer constant α, as either of the latter is proportional to $\mathcal{H}_{\text{new}}^2$. Similar remarks apply to III, IV. On the other hand, the contributions of I+II to α can be proved to be additive with respect to those of III+IV. Detailed calculation, of which we omit the details, shows that the transition probabilities due to III and IV are only of the order of magnitude 10^{-3} compared with those due to I and II. Hence we can safely disregard III and IV, as we do henceforth. In titanium, on the other hand, III was the main effect, and I and II were nonexistent, while IV was negligible in comparison with III, and so was neglected entirely. The reason that this was permissible is that in Ti, the important excited levels were separated from the ground state only in virtue of the splitting Δ due to the noncubic portion of the crystalline potential. Consequently the extra frequency denominator contained in III as compared with IV was Δ rather than the cubic splitting ν_{52}(or ν_{42}). So in Ti, the effect of III, instead of being comparable with IV as in Cr, was enhanced relative to IV by a factor ν_{52}/Δ in $\mathcal{H}_{\text{new}}$ or $(\nu_{52}/\Delta)^2$ in α.

We shall compute only the parts of I and II due to vibrations of the type Q_2, Q_3. This restriction suffices to fix approximately the order of magnitude of the relaxation time, and very materially simplifies the calculation because Q_2, Q_3 do not give rise to any matrix elements joining Γ_2 with Γ_4 or Γ_5. A more complete calculation, where all types of vibration are fully considered, would be quite laborious, and does not seem warranted at the present time.

In order to compute the result of the mechanism I, with the above simplifications, it is necessary to have besides the matrix elements of the orbit-lattice energy internal to Γ_5 given in (21) and (22d) of l.c., also those of type Q_2, Q_3 joining Γ_4 and Γ_5. The latter can be shown to be

$$\mathcal{H}_{OL}(\Gamma_{4a};\Gamma_{5a})=-2pQ_2,\quad \mathcal{H}_{OL}(\Gamma_{4b};\Gamma_{5b})=p(Q_2-\sqrt{3}Q_3),\quad \mathcal{H}_{OL}(\Gamma_{4c};\Gamma_{5c})=p(Q_2+\sqrt{3}Q_3),$$

with $p=[-3\rho_1+(25/44)\rho_2]/\sqrt{15}$.

To calculate the influence of II, one makes use of the fact that expansion of the crystalline potential given in (9) of l.c. to the second order has the effect of replacing ρ_2Q_2, ρ_2Q_3, respectively, by

$$\rho_2Q_2-7\rho_2R^{-1}Q_2Q_3/2\sqrt{3},\quad \rho_2Q_3-7\rho_2R^{-1}(Q_2^2-Q_3^2)/4\sqrt{3},$$

in (21) of l. c., providing we neglect all terms involving other coordinates than Q_2, Q_3.

In essentially the same way that we obtained (48), except that the perturbation theory is carried one order higher, we find for the transformed Hamiltonian function involving the effect of I and II

$$\mathcal{H}_{\text{new}}=E\{[Q_3^2-Q_2^2][2S_z^2-S_x^2-S_y^2]+2\sqrt{3}Q_2Q_3[S_x^2-S_y^2]\},\tag{59}$$

with

$$E=-\left[\frac{4\zeta^2}{h^3\nu_{52}{}^3}\right]\left[3\left(\frac{175}{396}\rho_2\right)^2-\frac{7}{4}\frac{h\nu_{52}}{R}\left(\frac{175}{396}\right)\rho_2-\frac{1}{15}\frac{h\nu_{52}}{h\nu_{42}}\left(-3\rho_1+\frac{25}{44}\rho_2\right)^2\right].$$

The calculation now proceeds in more or less the same fashion as in connection with the Raman terms for Ti, but with the difference that there is a splitting of the basic multiplet due to the crystalline potential as well as the applied field. However, solution of the secular problem can be avoided, as in the case of the direct processes for Cr, by expressing the results in the form of an invariant diagonal sum. Eqs. (51) and (52) are still applicable and it is finally found that the formula for the energy transfer constant is

$$\alpha=GNI_6k^{-1}T^{-2}R^4(16\pi^2EV/15M)^2(v_l{}^{-5}+\tfrac{3}{2}v_t{}^{-5})^2,\tag{60}$$

TABLE I. *Relaxation time for chrome alum due to Raman process.*

	$H_0=0$	800	1600	2400	3200	∞ GAUSS
$\tau_{\text{calc}}\times 10^6$ (90°K)	0.14	0.18	0.22	0.24	0.26	0.28
$\tau_{\text{obs}}\times 10^6$ (90°K)		0.06	0.12	0.16	0.19	
$\tau_{\text{calc}}\times 10^6$ (64.4°K)	0.43	0.56	0.70	0.77	0.80	0.86
$\tau_{\text{obs}}\times 10^6$ (64.4°K)		0.53	0.76	0.92	1.02	

where I_6 is defined as in (39), and

$$G=\text{spur}\,[(2S_z^2-S_x^2-S_y^2)W-W(2S_z^2-S_x^2-S_y^2)]^2+3\,\text{spur}\,[(S_x^2-S_y^2)W-W(S_x^2-S_y^2)]^2. \quad (61)$$

Here, W is the matrix (55) of the Hamiltonian function representing the combined energy due to the Zeeman effect and the crystalline potential. Explicit computation of G gives

$$G=72h^2\Delta\nu^2[1+8(H\beta/h\Delta\nu)^2]. \quad (62)$$

We can now calculate the relaxation times with the aid of (58), (60), (62) and numerical values of the constants as stated after (58). We shall multiply all estimates of τ thus obtained by a factor 1/10, as we have considered only the vibrations of the type Q_2, Q_3, and a rough calculation[19] shows that the transition probability will be increased by a factor of the order 10 when allowance is made for vibrations of the form Q_4,Q_5,Q_6, and for the interplay between Q_2,Q_3, and Q_4,Q_5,Q_6, etc. With this modification, the relaxation times which we calculate from our formulas at 90° and 64.4° are shown in Table I for various applied fields, along with recent experimental determinations made by Gorter and collaborators.[20] The agreement between the calculated and observed orders of magnitude of the relaxation time must be regarded as adequate in view of the approximate character of the theoretical model. The predicted dependence on temperature is obviously not rapid enough. The calculated ratios of the relaxation times at two different temperatures has theoretically a particularly simple origin, as it arises solely in virtue of the factor I_6 in (60), defined by (39). The diagreement is doubtless due mainly to the fact that the actual frequency spectrum for the lattice does not conform to the ω^2 law at high frequencies, and need not cause concern, since it is well known that the law fails badly in the vicinity of the cut-off frequency $k\theta/h$. Also in this region the assumption (11) that the wave-length is long compared with the radius R of the cluster $\text{Cr}\cdot 6\text{H}_2\text{O}$ is not warranted and the resulting error will change the temperature dependence somewhat. The discrepancies in the dependence of τ on the magnetic field appear to be more fundamental, as we shall see in Section VIII.

VIII. DEPENDENCE OF τ ON THE APPLIED MAGNETIC FIELD H_0

The calculated orders of magnitude of the relaxation time naturally depend on the numerical values selected for the various constants, such as (33). On the other hand, the predictions regarding the variation of τ with the applied field H_0 are of a very general character not contingent on how these constants are selected, or upon the approximation (11).

At liquid-air temperatures, where only the Raman processes are important, the relaxation time τ should theoretically depend on H_0 in the fashion

$$\tau=(1+d^2H_0^2)\tau_0/(1+c^2H_0^2) \quad (63)$$

as can be seen from Eqs. (58), (60), and (62). In (63), τ_0 is the relaxation time for zero field strength and d and c are constants. With our choice (33) of constants, d and c have, respectively, the values 1.2×10^{-3} and 0.85×10^{-3}

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[19] In this connection it should be mentioned that uneven vibrations of the type $Q_7, \cdots, Q_{15}$, defined in l.c., can contribute to the transition probability through the terms of the structure II described at the beginning of Section VII. This is true because the Taylor's expansion of the potential does not involve solely the even modes of vibration when quadratic terms are included. Also Q_1 can be involved in II, since proper choice of origin only eliminates the linear term in Q_1.

[20] I am much indebted to Professor Gorter for communicating these results in advance of publication.

gauss. As d is larger than c, the relaxation time should increase with field strength. The critical frequency region in which τ is most sensitive to H_0 is predicted correctly, but the calculated variation is not rapid enough (cf. Table I, Section VII). The latter discrepancy is not to be dismissed lightly, as theoretically the ratio $d^2/c^2=\tau_\infty/\tau_0$ has a value 2 quite irrespective[21] of the choice of values assigned the cubic splittings, the decomposition $\Delta\nu$ of the basic quartet, the vibrational amplitude, etc., whereas at 90° experimentally τ varies by a factor 3 when H_0 is increased from 800 to 3200 gauss. Possibly there may be some uncertainty in the empirical relaxation times, since the experimental points are fitted so as to make χ_ν in (27) extrapolate to the theoretical value $\chi_0(1-F)$ when $\nu=\infty$. Small departures of χ_∞ from the ideal value $\chi_0(1-F)$ are to be expected if the assumption of a spin temperature fails at the highest field strength at liquid-air temperatures, and this fact might alter slightly the variation with H_0 to be assigned to τ.

At helium temperatures, where the direct rather than Raman processes are important, the predicted dependence on field strength is entirely wrong. The values of d and c in (63) become, respectively, 1.2×10^{-3} and 1.6×10^{-3} gauss^{-1}, as one finds from (57) and (58) if one disregards the part of α' of the fourth order in H_0. As d is now considerably less than c, the relaxation time should decrease with field strength, in marked contradiction with the experimental data. To make matters worse, if the field strength is large ($\sim10^3$ gauss) we must, by (56), add to the denominator of (63) a term of the structure

$$e_1{}^4[H_{0_x}{}^4+H_{0_y}{}^4+H_{0_z}{}^4] + e_2{}^4[H_{0_x}{}^2H_{0_y}{}^2+H_{0_y}{}^2H_{0_z}{}^2+H_{0_z}{}^2H_{0_x}{}^2] \qquad (64)$$

with $e_1=0.78\times10^{-3}$, $e_2=0.88\times10^{-3}$ gauss^{-1}. These extra terms accentuate still further the theoretical decrease of relaxation time with increasing field strength.

The effect of Temperley

In an interesting paper, Temperley[22] has suggested that the difficulties regarding dependence on field strength, and of the incorrect orders of magnitude of the relaxation times calculated in previous investigation and still present for titanium at helium temperatures can be avoided by taking account of the fact that several atoms may reverse their spins simultaneously. Supposedly the heat transfer between the spin and lattice is thus enhanced, and if the applied field inhibits concerted action, an explanation is obtained of why the relaxation time increases with field strength. Unfortunately, we do not believe that the effect of Temperley exists to an appreciable extent *if the spins are really in thermal equilibrium with each other*. In our opinion his estimates of numerical orders of magnitudes are misleading because they do not take cognizance of the possibility of writing the answers as invariant diagonal sums not materially influenced by cluster formation. If his effect were important it would imply that the assumption that spin-spin interaction can be represented by a Gaussian distribution of internal magnetic fields, is grossly incorrect. It is possible to extend our calculations so as to incorporate the spin-spin interaction exactly, rather than by means of the hypothesis of an internal field, and hence to examine whether Temperley's mechanism really gives an essential modification of the results. We may for simplicity suppose that the phase of the Debye waves is the same for all the atoms of the crystal, for this assumption is the most favorable to the existence of the constructive interference between atoms presupposed by Temperley. We can regard the whole crystal as a structural unit. Then the new Hamiltonian function involves summation over all the

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[21] Strictly speaking, the statement that τ_∞/τ_0 can only have the value 2.0 is not true. Were we to consider Raman terms arising from Q_4, Q_5, Q_6 as well as merely from Q_2, Q_3, we would find that the transformed Hamiltonian function contained spin matrices of the type S_xS_y, S_yS_z, S_zS_x, like those associated with ϵ_2 in (48), whereas the function (59) which we use involves only those of the type connected with ϵ_1 in (48). (In the language of group theory, the ϵ_1, ϵ_2 structures appear according as the symmetrical direct product of the Q's corresponding to our Raman process has the transformation properties of the representation Γ_3 or Γ_5.) With the ϵ_2 type, α is proportional to $1+12(H\beta/h\Delta\nu)^2$ instead of (62). The Γ_3 and Γ_5 forms thus give upper and lower limits 2.5 and 1.7 for d^2/c^2 in (63). In constructing Table I and giving a numerical value for d in (63) we have assumed that the two structures contribute equally to α, so that α is proportional to $1+10(H\beta/h\Delta\nu)^2$. It may be that the lattice vibrations important for the ϵ_1 and ϵ_2 forms have a different frequency spectrum, and so a different temperature dependence. If so, d^2/c^2 can be a function of temperature, rather than a constant independent of T, as we have treated it to be. Actually d^2/c^2 does vary with T, but it is doubtful whether sufficient variation is given by our theory, for even under the most extreme assumptions the calculated variation would be only between 1.7 and 2.5. (In iron, the corresponding values are 1.7 and 4.5, so that there is more leeway.)

If the nonadiabatic terms were effective, $\mathcal{H}_{\text{new}}$ would be linear in the spin matrices, rather than quadratic, as in (48) or (59), and one can show that then in the Raman case in chromium we have $d^2/c^2=3.0$ in somewhat better agreement with experiment. However, as already mentioned, the nonadiabatic terms appear to be considerably smaller than the adiabatic ones. Kronig's study of the relation between transition probability and relaxation time (Physica **5**, 65 (1938)), which is a generalization to $S>\frac{1}{2}$ of the Kronig and Gorter article mentioned in note 13, assumed essentially a linear $\mathcal{H}_{\text{new}}$, so that his discussion applies to the nonadiabatic terms only.

[22] C. N. V. Temperley, Proc. Camb. Phil. Soc. **35**, 256 (1939).

paramagnetic atoms of the crystal instead of applying to a single atom. Thus the transfer constant is given by (53) or (60), but with the factor N deleted, and with the matrices S_z^2, S_xS_y etc. in the definitions (48) and (61) of $H^{(k)}$ and G replaced, respectively, by $\Sigma_i S_{zi}^2$, $\Sigma_i S_{xi}S_{yi}\cdots$, where the subscript i means that the spin in question relates to atom i. Also the quantity W is no longer defined as in (55), and is instead

$$W=\Sigma_i 2\beta \mathbf{H}_0\cdot\mathbf{S}_i+\Sigma V_i+\Sigma_{j>i}V_{ij}, \tag{65}$$

where V_{ij} is the spin-spin coupling (4) and V_i is the crystalline potential

$$V_i=\tfrac{1}{6}h\Delta\nu(S_{xi}+S_{yi}+S_{zi})^2.$$

Because of the fact that V_{ij} commutes with S_k unless $i=k$ or $j=k$ and because of the fact that

$$\text{Spur}\,[S_{zi}^2V_{ij}-V_{ij}S_{zi}^2][S_{zk}^2V_{kl}-V_{kl}S_{zk}^2],\ \text{etc.}$$

vanishes unless $i=k$, $j=l$ or $i=l$, $j=k$, one sees that interference between only two atoms at a time can be involved in (61), where W occurs quadratically. Since $(x+y)^2 \leqq 2x^2+2y^2$, this means that the interference effects can only double the calculated transition probability. Similarly, in (53), where W occurs biquadrically, one can show that only four atoms at a time will interfere, so that at most the amplification due to the Temperley effect is by a factor 4. Temperley, on the other hand, needed a cooperative effect inside a cluster containing about 300 atoms. Our estimates of the amount of interference in the spin-spin terms are only upper limits, and furthermore the main part of (65), results not from the dipolar coupling V_{ij}, but from the crystalline potential V_i whose contribution to the relaxation is purely additive from the various atoms. In consequence of the partial interference, the value of C in (63) is slightly changed, but we find that even on taking the extreme limits derived above, the alteration is nothing like sufficient to make $d/c>1$ for the direct process for chromium, as is required if the relaxation time is to increase with field strength at helium temperatures.

In the preceding discussion we have tacitly given the impression that our use of a Gaussian distribution of internal magnetic fields to represent the dipole-dipole coupling would be rigorous if we neglected the possibility of two or more spins reversing simultaneously. This is not really so in the calculation of the direct processes. Here the fourth power of the internal field or dipole-dipole interaction is involved, and the Gaussian law does not necessarily give the correct dispersion, i.e., it may not give the proper mean fourth power although it is adjusted to work on the square. Examination of an explicit calculation which the writer[23] has made of the mean fourth power in the somewhat related case of exchange coupling indicates that the resulting error is not serious. There is also a correction because of the fact that in computing the direct process for atom i the dipole interaction joining atoms i and j does not commute with the crystalline potentials V_j of atom j. Consequently atom i feels the crystalline potential of other atoms via the dipole-dipole coupling. The resulting modifications can be computed, but prove to be of minor importance, as well as in the wrong direction.

Possible explanations of the difficulty.—Since, in our opinion, the Temperley effect does not enter appreciably with the thermodynamic model, one looks for other reasons why our calculated dependence of τ on field strength is wrong at low temperatures. The most obvious suggestion is that the assumption of a spin temperature is not warranted, but any explanation of this character seems to be pretty well refuted by the usual conformity of the dispersion curves to formula (27), and especially by the fact that the empirical and theoretical values of the constant F in (27) agree so well. The incorrect dependence on field strength is due to the factor ω^2 in the frequency spectrum (19) of the lattice oscillators. This factor makes the energy transfer constant α for the direct processes proportional to the fourth power of the energy quantum ΔW exchanged between spin and lattice, whereas only the square occurs in the case of the Raman mechanism (cf. Eqs. (53) and (61)). The applied field modulates $(\Delta W)^4$ to a greater extent than it does $(\Delta W)^2$, (e.g. the coefficient of H^2 is six times as large in an expression of the form $(1+xH_0)^4$ as for $(1+xH_0)^2$). So in the direct process the increase of α $(=\alpha_0[1+d^2H_0^2])$ with H_0 is so great as to more than offset the corresponding increase of the specific heat C_H $(=C_0[1+c^2H^2])$, whereas with the Raman mechanism this is not true. Since $\tau=C_H/\alpha$, the sign of $d\tau/dH_0$ is thus different in the two cases. The troublesome ω^2 factor would be removed if at low temperatures the spins owed their heat contacts to conduction electrons rather than lattice oscillators, but apparently the apparatus actually does not have important metallic connections.

Another interesting but highly conjectural possibility is that the use of the conventional distribution law $\rho_\omega\sim\omega^2$ for lattice oscillators is not warranted at exceedingly low frequencies. Undoubtedly this law would be accurate for infinitely small vibrations of small ω, but the zero-point energy requires finite amplitudes, which are particularly large for the vibrations of lowest frequency (cf. Eq. (14)). Hence the anharmonic corrections may make the distribu-

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[23] J. H. Van Vleck, Phys. Rev. **55**, 927 (1939).

tion materially different from the usual idealized form. Similar remarks apply to the effect of disturbances caused by contact of the oscillators with the "walls" (e.g. helium bath). If the interruptions are sufficiently rapid, ω loses meaning and the frequency distribution is blurred out, diminishing the apparent dependence of ρ_ω on ω. Conceivably the oscillations most active in modulating the cluster $Cr\cdot 6H_2O$ are not typical of the crystal as a whole and have a different distribution law. If ρ_ω could for our purposes be treated as independent of ω for low values of ω, then the dependence of τ on H_0 would be the same for the direct as for the Raman processes and we would have in either case $d\tau/dH_0>0$, as desired.

Dependence on direction of applied field.—Experiments on the dependence of τ on the direction of the applied field at helium temperatures are not yet available but would be particularly desirable because of the light which they would throw on the preceding considerations. According to our calculations of the relaxation due to the direct processes with the usual frequency distribution law (19), τ should exhibit some anisotropy at helium temperatures at high field strengths, because of the addition of (64) to the denominator of (63). The resulting anisotropy is small, amounting to about 10 percent in fields of 3000 gauss or greater, but is not beyond detection in refined experiments (unlike the negligible anisotropy calculated in Section III for the direct processes in titanium). On the other hand, if the ω^2 factor due to the frequency distribution law (19) is removed, as we suggested in the preceding paragraph, then τ becomes isotropic even for the direct processes.

The calculation of Section VII (or of Section III for titanium) show that the relaxation times due to the Raman mechanism do not depend on the direction of the applied field. This prediction is in accord with experiments made by Teunissen and Gorter at liquid-air temperatures.[24]

IX. Iron Alum

There are more extensive experimental data on paramagnetic dispersion for iron than for chrome alum, but the theory of the Stark decomposition for the basic state of the Fe^{+++} ion is somewhat ambiguous. For this reason we have made our detailed calculations on Cr^{+++}. Still there is a certain parallelism between the two ions. The temperature dependence is governed by similar factors, and in particular our conclusions in Section VIII regarding the dependence on field strength should also apply to Fe^{+++}. There is still the difficulty that $d\tau/dH_0$ has the wrong sign at helium temperatures. In the Raman processes characteristic of the liquid-air region, the calculated values of the ratio d^2/c^2 connected with (63) range from 1.7 to 4.5, depending on the assumption one makes concerning the nature of the crystalline field and the type of vibration effective.[25] The most likely value is in the neighborhood of 2.5. The computed ratios are thus somewhat larger than for chromium and so give somewhat better agreement with the experimental dependence on field strength than that shown in Table I for chromium.

As regards orders of magnitude, one should expect the Raman τ to be roughly of the same size in iron as for chromium. This prediction agrees with observation. On the other hand, the direct processes occur in iron only if one includes matrix elements nondiagonal in the principal quantum number, or else retains higher powers of the spin-orbit interaction than in chromium.[26] So it is hard to understand why τ at helium temperatures is not experimentally markedly larger for iron than for chromium.

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[24] Teunissen and Gorter, Physica **5**, 855 (1938); (measurements on iron alum, but our prediction of isotropy still applies).

[25] It is uncertain whether the splitting of the spin components of the basic state of the iron ion is due primarily to the cubic or axial (trigonal) members of the crystalline potential. There is no similar ambiguity in chromium, since a cubic field cannot decompose the basic state of Cr^{+++}. For a cubic field in iron alum the value of $d^2/c^2 = \tau_\infty/\tau_0$ characteristic of the ϵ_1 and ϵ_2 structures cited in note 21 are, respectively, 1.7 and 4.5. For a second-order axial field of type $x^2+y^2-2z^2$ the corresponding values are 2.7 and 2.2. If, as in Section VIII, it is assumed that the ϵ_1 and ϵ_2 forms contribute equally to α_0, then the appropriate mean values for the cubic and axial cases are, respectively, 2.5 and 2.4. These estimates are inclusive of the effect of the contributions of the spin-spin field K to α_0 and C_H, which are very much more important than in chromium. (If we could set $K=0$, the maximum value of τ_∞/τ_0 would be 6.25 rather than 4.5). Teunissen's data, reference 1, give some evidence that τ_∞/τ_0 is lower experimentally for iron nitrate than for the alums, as is perhaps reasonable since the nitrates have rhombic rather than cubic symmetry.

[26] See C. J. Kynch, Trans. Faraday Soc. **33**, 1402 (1937), also J. H. Van Vleck and W. G. Penney, Phil. Mag. **17**, 961 (1934) concerning vanishing of matrix elements in half-completed shells.