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Chemical Effects in Nuclear Magnetic Resonance and in Diamagnetic Susceptibility*

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An expression for the magnetic shielding of nuclei in solids and in molecules is developed, and an approximation is obtained that is particularly suited to substances containing heavy atoms. The temperature dependence of the magnetic shielding which arises when there are several low-lying states of the molecules is discussed. It is shown that only slight changes in the various formulas make them applicable to the diamagnetic susceptibility.

1. INTRODUCTION

IN the author's original paper[1] on chemical shifts and magnetic shielding, the development was limited to systems which on the average were cylindrically symmetric about the direction of the magnetic field, such as molecules in states whose axis of quantization was parallel to the magnetic field. A more general expression not subject to this limitation and hence applicable to crystals is obtained in the present paper.

In the earlier paper,[1] the general expression for the shielding [Eq. (6) of that paper[1]] contained two apparently quite different types of terms, each of which would have to be calculated separately by approximate methods in actual problems. In the present paper, it is shown that by a suitable gauge transformation an alternative approximate form for this expression can be obtained in which one of these types of terms (the second-order paramagnetism terms) vanish for electrons tightly bound to any of the atoms in the molecule.

Finally, in the earlier paper,[1] it was assumed that there were no alternative states separated from the ground state by an energy comparable to kT for which the magnetic shielding was different. Consequently, no temperature dependence of the shielding was indicated. Although for most molecules this assumption is valid and the magnetic shielding is temperature independent, a few cases of temperature dependent magnetic shielding have been observed. The treatment of the present paper will cover such cases as well and, in addition, is applicable to the temperature dependence of the diamagnetic susceptibility.

2. MAGNETIC SHIELDING CALCULATION

Consider a polyatomic molecule or crystal which in the absence of an external field has no resultant electron spin or electron orbital angular momentum. Since the nuclei are massive compared to the electrons, the nuclei can be treated classically to a very good approximation. In particular, in the first phases of the calculation the nuclei will be considered to be approximately stationary, attracting centers whose orientation is specified by λ. As is discussed in the earlier paper,[1] the effects of electron spin can be omitted in the subsequent discussion; except in cases of accidental degeneracies, the magnetic shielding fields from the electron spins should be of higher orders of smallness than the other contributions calculated here. It should be noted, however, that this result arises from the fact that magnetic shielding by definition is concerned only with effects proportional to the external magnetic field **H**. Consequently, any direct contribution of the electron spins to the shielding field which arises in a second-order perturbation calculation will depend on matrix elements of the interaction between **H** and the electron spins which are nondiagonal in the resultant electron spin. If, however, **H** is uniform over the entire molecule such matrix elements vanish. As recently discussed by Ramsey and Purcell[2] while considering the shielding of the interaction between two nuclear magnetic moments in the same molecule, the effect of the electron spins must be included when **H** is not uniform over the molecule.

If the origin of the coordinate system is taken at the nucleus where the shielding is to be evaluated, if $\boldsymbol{\mu}$ is the magnetic moment of that nucleus, and if **H** is the external magnetic field, the vector potential for the kth electron at position $\mathbf{r}_k$ may be taken as

$$\mathbf{A}_{kl}=\tfrac{1}{2}\mathbf{H}\times\mathbf{r}_k+\boldsymbol{\mu}\times\mathbf{r}_k/r_k^3-\tfrac{1}{2}\mathbf{H}\times\mathbf{R}_{kl}, \qquad (1)$$

where $\mathbf{R}_{kl}$ is a purely arbitrary constant and arises from the arbitrariness of the gauge of the vector potential. With this vector potential and with $(-e)$ as the charge of the electron, the Hamiltonian operator for the electrons of the system is

$$\mathcal{H}=\sum_{k=1}^{n}\frac{1}{2m}\left[\frac{\hbar}{i}\nabla_k+\frac{1}{2}\frac{e}{c}\mathbf{H}\times[\mathbf{r}_k-\mathbf{R}_{kl}]+\frac{e}{c}\frac{\boldsymbol{\mu}\times\mathbf{r}_k}{r_k^3}\right]^2+V. \qquad (2)$$

By an expansion and a few simple transformations of vector products, this can be written as

$$\mathcal{H}=\mathcal{H}^{(0)}+\mathcal{H}^{(1)}+\mathcal{H}^{(2)}, \qquad (3)$$

where

$$\begin{aligned}\mathcal{H}^{(0)}&=-\textstyle\sum_k(\hbar^2/2m_k)\nabla_k^2+V,\\ \mathcal{H}^{(1)}&=-\textstyle\sum_k \mathbf{H}\cdot\mathbf{m}_{kl}^0-\sum_k 2\boldsymbol{\mu}\cdot\mathbf{m}_{k0}^0/r_k^3, \qquad (4)\\ \mathcal{H}^{(2)}&=(e^2/8mc^2)\textstyle\sum_k(\mathbf{H}\times[\mathbf{r}_k-\mathbf{R}_{kl}]+2\boldsymbol{\mu}\times\mathbf{r}_k/r_k^3)^2,\end{aligned}$$

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[1] N. F. Ramsey, Phys. Rev. **77**, 567 (1950) and **78**, 699 (1950).

[2] E. M. Purcell and N. F. Ramsey (to be published).

with

$$\mathbf{m}_{kl}{}^{0} = -(e\hbar/2mci)[\mathbf{r}_k - \mathbf{R}_{kl}] \times \nabla_k$$

and

$$\mathbf{m}_{k0}{}^{0} = -(e\hbar/2mci)\mathbf{r}_k \times \nabla_k. \tag{5}$$

Therefore, by the usual second-order perturbation theory[1, 3] and by use of the well-known transformation reducing the scalar product of two vector products, if W_λ' is the sum of the energy terms linear in $\boldsymbol{\mu}$ and $\mathbf{H}$, one obtains

$$W_\lambda' = \boldsymbol{\mu} \cdot \boldsymbol{\sigma}_\lambda{}^{d} \cdot \mathbf{H}, \tag{6}$$

where $\boldsymbol{\sigma}_\lambda{}^{d}$ is the dyadic

$$\begin{aligned}\boldsymbol{\sigma}_\lambda{}^{d} = (e^2/2mc^2)(n\lambda|\textstyle\sum_k\{\mathbf{1}^{d}(\mathbf{r}_k - \mathbf{R}_{kl})\cdot\mathbf{r}_k \\ -(\mathbf{r}_k - \mathbf{R}_{kl})\mathbf{r}_k\}/r_k{}^3|n\lambda) - 4\,\mathrm{Re}\textstyle\sum_{n'\lambda'}[1/(E_{n'}-E_n)] \\ \times[(n\lambda|\textstyle\sum_k \mathbf{m}_{k0}{}^0/r_k{}^3|n'\lambda')(n'\lambda'|\mathbf{m}_{kl}{}^0|n\lambda)].\end{aligned} \tag{7}$$

It is of interest to note that the terms of the first type in (7) can be given a simple physical interpretation. If an electron at position $\mathbf{r}_k$ moves with angular velocity $\boldsymbol{\omega}$ about a point $\mathbf{R}_{kl}$, then the magnetic field at the origin resulting from this motion is

$$\begin{aligned}\mathbf{H}' &= -(e/c)[\boldsymbol{\omega}\times(\mathbf{r}_k - \mathbf{R}_{kl})]\times\mathbf{r}_k/r_k{}^3 \\ &= [\{e^2/2mc^2\}\{\mathbf{1}^{d}(\mathbf{r}_k - \mathbf{R}_{kl})\cdot\mathbf{r}_k \\ &\qquad -(\mathbf{r}_k - \mathbf{R}_{kl})\mathbf{r}_k\}/r_k{}^3]\cdot[2mc\boldsymbol{\omega}/e].\end{aligned} \tag{8}$$

Therefore, the terms of the first part of (7) correspond to the magnetic field at the position of the nucleus being shielded by circulations of the electrons about the points $\mathbf{R}_{kl}$ with angular velocity $e\mathbf{H}/2mc$. As the points $\mathbf{R}_{kl}$ are arbitrary, the axes of the circulation are therefore arbitrary. At first sight this seems surprising, since the magnitude of the field clearly depends on the location of this axis. The explanation of this apparent anomaly is that $\mathbf{R}_{kl}$ also enters in the terms of the second type since $\mathbf{m}_{kl}{}^0$ depends on $\mathbf{R}_{kl}$, and any changes in the terms of the first type which result from a change in the values of $\mathbf{R}_{kl}$ are just exactly compensated by the corresponding changes in the terms of the second type. It should, of course, be noted that expression (7) provides only the electronic magnetic shielding contribution to shifts in nuclear resonance frequencies. In molecules in specific orientation states and in crystals, there are also, in general, much larger and more conspicuous shifts because of magnetic interactions of the nuclear spins, nuclear quadrupole interactions, etc. In general these depend differently on the external field than does the magnetic shielding, and their effects can be calculated by well-established methods.[4, 5]

In many problems only a single component of the dyadic, say the zz component, is of interest. This is the case, as an example, for a molecule in the presence of a magnetic field along the z axis in case the orientation state of the molecule is on the average symmetrical about the z axis, as when it is specified by the magnetic quantum number relative to that axis. However, even for crystals, if only the magnitude of the field at the nucleus is of interest, it is given to the first approximation by the zz component of the dyadic only. If the zz component of $\boldsymbol{\sigma}_\lambda{}^{d}$ is called σ_λ, Eq. (7) gives

$$\begin{aligned}\sigma_\lambda = (e^2/2mc^2)(n\lambda|\textstyle\sum_k\{(x_k - X_{kl})x_k \\ +(y_k - Y_{kl})y_k\}/r_k{}^3|n\lambda) \\ -4\,\mathrm{Re}\textstyle\sum_{n'\lambda'}{}'[1/(E_{n'}-E_n)] \\ \times[(n\lambda|\textstyle\sum_k m_{zk0}{}^0/r_k{}^3|n'\lambda')(n'\lambda'|m_{zkl}{}^0|n\lambda)].\end{aligned} \tag{9}$$

It should be noted that if $\mathbf{R}_{kl}$ is taken as zero the above result is that given in the previous papers.[1, 3] In fact, one can derive (9) in an alternative fashion by starting with Eq. (6) of the earlier paper,[1] which was based on a particular gauge corresponding to $\mathbf{R}_{kl}=0$, and by transforming the coordinates to express the angular momentum $(-2mc/e)m_{zk}{}^0$ about the origin in terms of the angular momentum about the point $\mathbf{R}_{kl}$ in a fashion similar to that of Van Vleck[6] in showing the invariance of the magnetic susceptibility of molecules to the choice of the origin.

If the problem, in addition to being cylindrically symmetric about the field, is also on the average spherically symmetric as when all states of different possible magnetic quantum numbers are equally occupied, Eq. (9) reduces on the average to

$$\begin{aligned}\sigma_\lambda = (e^2/3mc^2)(n\lambda|\textstyle\sum_k\{(1/r_k) - (\mathbf{R}_{kl}\cdot\mathbf{r}_k/r_k{}^3)\}|n) \\ -(4/3)\,\mathrm{Re}\textstyle\sum_{n'}{}'[1/(E_{n'}-E_n)] \\ \times[(n|\textstyle\sum_k \mathbf{m}_{k0}{}^0/r_k{}^3|n')\cdot(n'|\mathbf{m}_{kl}{}^0|n)].\end{aligned} \tag{10}$$

3. MOLECULES WITH HEAVY ATOMS

The previous expressions have the disadvantage that all electrons in the molecule or crystal must be included in the calculation, even though it is physically apparent that electrons tightly bound to distant nuclei will make only a small contribution. In the above formulation this result is achieved by virtue of the terms of the first type in (7) approximately canceling terms of the second type for such electrons. Since, however, in most problems each type of term would be calculated only approximately, it is important to obtain an expression in which the result for such electrons does not appear as a very small difference in two large approximately calculated quantities.

Let N_K electrons form complete shells that are so tightly bound to the Kth nucleus that their mean potential is approximately spherically symmetric about the Kth nucleus, and let N_S electrons be all the remaining electrons which cannot be considered to be bound overwhelmingly to any single atom in the molecule. Then select $\mathbf{R}_{kl}$ to be $\mathbf{R}_K$, the radius vector to the Kth nucleus, if k corresponds to one of the N_K electrons tightly bound to the Kth nucleus, and let

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[3] N. F. Ramsey, Phys. Rev. **83**, 540 (1951).

[4] Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. **57**, 677 (1940).

[5] R. V. Pound, Phys. Rev. **79**, 685 (1950).

[6] J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), pp. 275–276.

$\mathbf{R}_{kl}$ remain arbitrary for the N_S electrons not tightly bound to any nucleus. With this selection and with the spherical symmetry of the potential about the Kth nucleus, there will be no nondiagonal matrix elements of the orbital angular momentum operator $(-2mc/e)\mathbf{m}_{kK}$ about the Kth nucleus for any of the N_K electrons tightly bound to the Kth atom. Consequently, Eq. (7) reduces approximately to the following expression,

$$\begin{aligned}\boldsymbol{\sigma}_\lambda = (e^2/2mc^2)\sum_K (n_K\lambda|\sum_{k=1}^{N_K}\{\mathbf{1}^d(\mathbf{r}_k-\mathbf{R}_K)\cdot\mathbf{r}_k \\ -(\mathbf{r}_k-\mathbf{R}_K)\mathbf{r}_k\}/r_k{}^3|n_K\lambda) \\ +(e^2/2mc^2)(n_s\lambda|\sum_{k=1}^{N_S}\{\mathbf{1}(\mathbf{r}_k-\mathbf{R}_{kl})\cdot\mathbf{r}_k \\ -(\mathbf{r}_k-\mathbf{R}_{kl})\mathbf{r}_k\}/r_k{}^3|n_s\lambda) \\ -4\,\mathrm{Re}\sum_{n_s'\lambda'}[1/(E_{ns'}-E_n)] \\ \times[(n_s\lambda|\sum_{k=1}^{N_S}\mathbf{m}_{k0}/r_k{}^3|n_{s'}\lambda')(n_s'\lambda'|\mathbf{m}_{kl}{}^0|n_s\lambda)]. \quad (11)\end{aligned}$$

For the tightly bound electrons, therefore, the high frequency or second-order paramagnetic terms vanish. Equation (11) can be reduced to forms similar to (9) and (10) if the appropriate symmetries are applicable.

In the preceding paragraph the electrons were treated as if they were distinguishable, despite the fact that the wave functions must be antisymmetric in all the electrons. However, a similar result to the above can be obtained in a more complicated fashion if one adopts any of the methods of treating molecules in a suitably antisymmetric fashion, such as that of Slater,[7] provided the wave functions of the electrons tightly bound to any nucleus are approximately orthogonal to the remaining wave functions.

4. TEMPERATURE DEPENDENCE

The previous discussion has all been for a single electronic ground state n of the molecule. For most molecules, there is only a single electronic state possible within an energy range at all comparable to kT from the ground state, so that the previous expressions apply directly to most molecules and the magnetic shielding should be independent of the temperature, as usually is found to be the case.[8]

However, it has been found experimentally by Proctor and Yu,[8] and by Packard and Arnold[9] that in some cases there is a temperature dependence of the magnetic shielding. From the point of view of the above analysis, this presumably corresponds to there being several low-lying states for each of which the shielding, σ, is slightly different. Then, as the temperature is changed, the distribution between the states, and consequently, the average value of σ are altered.

The form of the temperature dependence to be anticipated can readily be obtained for any of the above shielding expressions. Since the cases in which temperature dependent effects have been observed are those which are such that on the average the distribution of the molecular orientation is spherically symmetric, only the temperature dependence that should arise from (10) will be discussed.

Assume that for states $n=0, 1, \cdots, g$ the quantity $\exp(-E_n/kT)$ is appreciable, while for the remaining states it is negligible. Then the weighted mean average of σ can be written as,

$$\sigma=\sigma_1+\sigma_2+\sigma_3,$$

where

$$\begin{aligned}\sigma_1 &= C\sum_{n=0}^{g}\exp(-E_n/kT)(e^2/3mc^2) \\ &\quad\times(n|\textstyle\sum_k\{(1/r_k)-(\mathbf{R}_{kl}\cdot\mathbf{r}_k/r_k{}^3)\}|n), \\ \sigma_2 &= -\frac{4}{3}C\,\mathrm{Re}\sum_{n=0}^{g}\exp(-E_n/kT)\sum_{n'=g+1}^{\infty}[1/(E_{n'}-E_n)] \\ &\quad\times[(n|\textstyle\sum_k\mathbf{m}_{k0}{}^0/r_k{}^3|n')\cdot(n'|\textstyle\sum_k\mathbf{m}_{kl}{}^0|n)], \quad (12) \\ \sigma_3 &= -\frac{4}{3}C\,\mathrm{Re}\sum_{n=0}^{g-1}\sum_{n'=n+1}^{g}[\exp(-E_n/kT) \\ &\quad-\exp(-E_{n'}/kT)][1/(E_{n'}-E_n)] \\ &\quad\times[(n|\textstyle\sum_k\mathbf{m}_{k0}{}^0/r_k{}^3|n')\cdot(n'|\textstyle\sum_k\mathbf{m}_{kl}{}^0|n)]\end{aligned}$$

and where,

$$C=1/\sum_{n=0}^{g}\exp(-E_n/kT).$$

It should be noted, however, that a single sharp line will be observed at the shifted frequency only if a molecule makes transitions between the different states $n=0, 1, \cdots, g$ at a sufficiently rapid rate that the Larmor precession of the nucleus occurs in the average field at the nucleus. In other words, collision narrowing[10] needs to occur. As discussed by Purcell, Bloembergen, and Pound,[10] if τ_c, the correlation time for the transitions, is short, the width of the resonance will be of the order $4\tau_c/\pi T_2''$,[2] where T_2'' is the transverse relaxation time in the absence of collision narrowing, so $1/T_2''$ is of the order of $\gamma H\Delta\sigma$ where $\Delta\sigma$ is the spread of the σ-values among the g lowest states. Therefore, the resonance width in the presnt case from this effect alone will be $4(\gamma H\Delta\sigma)^2\tau_c/\pi$.

The first reported temperature-dependent magnetic-shielding constants were those of the cobalt nucleus in $K_3Co(CN)_6$, $Co[C_2H_4(NH_2)_2]_3Cl_3$, and $Co(NH_3)_6Cl_3$, which were shown by Proctor and Yu[8] to be such that for a temperature increase from 20°C to 80°C the resonance frequency increased by 0.015 percent or about 1 kc out of 7000 kc. In these same molecules the chemical

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[7] J. C. Slater, Phys. Rev. 38, 1112 (1931).

[8] W. G. Proctor and F. C. Yu, Phys. Rev. 81, 20 (1951).

[9] M. E. Packard and J. T. Arnold, Phys. Rev. 83, 210 (1951).

[10] Purcell, Bloembergen, and Pound, Phys. Rev. 73, 704 (1947).

shift is large, with the resonance frequency for the last being 1.0083 times that of the first. The simultaneous occurrence both of the large chemical shift and of the temperature dependence indicates the existence of low-lying levels. Unfortunately, not enough data on the experimental temperature dependence are available as yet to determine the energy of the levels. However, the sign of the shift is enough to eliminate one very simple and attractive possibility. This possibility is that there might be only a single low-lying state in addition to the ground state, and that the existence of this level might be responsible both for the temperature dependence and for the large magnitude of σ which would then be chiefly the result of σ_3. In this case Eq. (12) would reduce approximately to

$$\sigma_3=-(4/3)\,\mathrm{Re}[1/(E_1-E_0)][(0|\textstyle\sum_k \mathbf{m}_{k0}{}^0/r_k{}^3|1)$$

$$\cdot(1|\textstyle\sum_k \mathbf{m}_{kl}{}^0|0)]\left[\dfrac{1-\exp\{-(E_1-E_0)/kT\}}{1+\exp\{-(E_1-E_0)/kT\}}\right]. \quad (13)$$

If this relation applied, E_1-E_0 could be calculated from the temperature dependence and $(0|\sum \mathbf{m}_{k0}{}^0/r_k{}^3|1)\cdot(1|\sum \mathbf{m}_k{}^0|0)$ could be calculated from the data. However, (13) would lead to a decrease in resonance frequency with increasing temperature which is just opposite to the observed results[8] with the cobalt compounds. Therefore, the simple relation (13) is not applicable in this case and the more complicated general relation (12) must be used.

The other important temperature shift so far reported is that of Packard and Arnold,[9] in which they observe in ethyl alcohol that the resonance of the hydrogen in the OH radical shifts markedly with temperature even though the magnitude of the shift itself is not unusually large. This suggests that the shift is not because of terms of the type σ_3 but instead to terms of the type σ_1 and σ_2. Liddel and Ramsey[11] have recently suggested a mechanism for the production of suitable low-lying alternative states in the process of molecular association in the liquid. Such association is usually assumed to be via a hydrogen bond affecting the hydrogen in OH, so it is quite reasonable that this hydrogen should be the one to have its temperature affected. It is important to note that since this mechanism depends on the molecular association of several molecules, it is dependent on the concentration of the liquid. Therefore, the temperature dependence will not be given simply by Eq. (12) which was derived for a single molecule. Instead, the various theories[12,13] for the equilibrium of the association must be used. The temperature dependence of the magnetic shielding in this case should in fact provide experimental information on the temperature dependence of the association equilibrium.

5. DIAMAGNETIC SUSCEPTIBILITIES

If the dyadic, $\boldsymbol{\xi}^d$, is the diamagnetic susceptibility of the molecule or crystal, expressions for $\boldsymbol{\xi}^d$ can be obtained analogous to each of the preceding formulas for $\boldsymbol{\sigma}^d$ provided only that in each expression for $\boldsymbol{\sigma}^d$ the $r_k{}^3$'s that occur are replaced by unity, except that in Eqs. (10) and (12) $1/r_k$ is also replaced by $r_k{}^2$. Thus, (10) with $\mathbf{R}_{kl}$ set equal to zero leads to a diamagnetic expression similar to that of Van Vleck.[6] As a further example, the diamagnetic susceptibility of a molecule with g low-lying excited states is given by the following expression corresponding to (12),

$$\xi=\xi_1+\xi_2+\xi_3, \quad (14)$$

where

$$\xi_1=C\sum_{n=0}^{g}\exp(-E_n/kT)(e^2/3mc^2)$$

$$\times(n|\textstyle\sum_k\{r_k{}^2-\mathbf{R}_{kl}\cdot\mathbf{r}_k\}|n),$$

$$\xi_2=-(4/3)C\,\mathrm{Re}\sum_{n=0}^{g}\exp(-E_n/kT)\sum_{n'=g+1}^{\infty}[1/(E_n-E_0)]$$

$$\times[(n|\textstyle\sum_k \mathbf{m}_{k0}{}^0|n')(n'|\sum_k \mathbf{m}_k{}^0|n)],$$

$$\xi_3=-(4/3)C\,\mathrm{Re}\sum_{n=0}^{g-1}\sum_{n'=n+1}^{g}[\exp(-E_n/kT)$$

$$-\exp(-E_{n'}/kT)][1/(E_{n'}-E_n)]$$

$$\times[(n|\textstyle\sum_k \mathbf{m}_{k0}{}^0|n')\cdot(n'|\sum_k \mathbf{m}_{kl}{}^0|n)].$$

Measurements of the diamagnetic susceptibilities of the cobalt molecules such as $K_3Co(CN)_6$ for which the magnetic shielding is temperature dependent[8] would be of great interest, as Van Vleck[14] has also pointed out. The diamagnetic susceptibility would presumably be temperature dependent as well, with the nature of the dependence being given by (14), in contrast to the usual observations that such susceptibilities are temperature independent. In fact, (14) provides an expression for the temperature dependence of the susceptibility that is frequently called the temperature independent paramagnetism.

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[11] U. Liddel and N. F. Ramsey, J. Chem. Phys. (to be published).

[12] J. H. Hildebrand and R. L. Scott, *Solubility of Non-Electrolytes* (Rheinhold Publishing Corporation, New York, 1950), p. 192.

[13] O. Redlich and A. T. Kister, J. Chem. Phys. **15**, 854 (1947).

[14] J. H. Van Vleck, Physica **17**, 281 (1951).