TEMPERATURE DEPENDENCE OF THE MAGNETIC HYPERFINE INTERACTION FOR IMPURITY ATOMS IN METALLIC FERROMAGNETS

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The temperature dependence of the magnetic field at Sn^{119} impurity atomic nuclei in Fe or Ni matrices has been measured by means of the Mössbauer effect. A large discrepancy has been found between the magnetic-field temperature dependence and the matrix-magnetization temperature dependence. This discrepancy is much larger for Sn in Fe than for Sn in Ni. A simple model is proposed which explains the anomalies observed in the temperature dependence of the magnetic hyperfine interaction. The model also explains some other results of the investigation of magnetic fields on nuclei of nonmagnetic impurity atoms in metallic ferromagnets. The experimental data are interpreted on the basis of the results of[5], according to which the field on the nucleus of an impurity nonmagnetic atom is the sum of two contributions of opposite sign. The anomalies in the temperature dependence of the magnetic field result from the change in the relative contributions with change in temperature. The anomalies are particularly pronounced for Sn impurity atoms, since in this case, both contributions to the field are almost equal in absolute value and hence almost compensate each other.

1. INTRODUCTION

THE study of the temperature dependence of the magnetic hyperfine interaction can give important information on the mechanisms of the origin of magnetic fields on atomic nuclei in ferromagnets. In pure metallic ferromagnets (Fe, Co, Ni) the temperature dependences $h(T)$ and $m(T)$ are practically identical. ($h(T) = H(T)/H(0)$, $m(T) = M(T)/M(0)$, where H is the magnetic field at the atomic nucleus, M the magnetization of the ferromagnetic matrix). For impurity atoms in metallic ferromagnetic matrices, significant discrepancies between $h(T)$ and $m(T)$ have been observed in a number of cases. If the impurity atom has a characteristic magnetic moment in the ferromagnetic matrix, these discrepancies can be explained on the basis of the molecular field model.[1] For nonmagnetic impurity atoms, such a model is inapplicable. Furthermore, for nonmagnetic atoms, significant discrepancies between $h(T)$ and $m(T)$ should not be expected, from general consideration. The only known mechanism which can produce a stronger temperature dependence of the reduced magnetic field (T) for a nonmagnetic impurity atom, in comparison with the magnetization of the matrix, is connected with a change in the mean magnetization of the atoms of the matrix near an impurity.[2,3] However, only small discrepancies can be explained by this mechanism, discrepancies which do not exceed several percent, while Jain and Cranshaw[4] have recently observed very large differences between $h(T)$ and $m(T)$ for Sn impurity atoms in a Co matrix.

In the present work, the temperature dependences of the magnetic fields at Sn^{119} impurity atomic nuclei in Fe and Ni matrices. It was observed that in these cases also, the dependence of $h(T)$ for Sn differs significantly from the temperature dependence of the magnetization of the matrices. The results (and also the results of several other experiments) are interpreted by means of very simple physical representations, based on the model proposed earlier[5] of the origin of a magnetic field on impurity atomic nuclei in metallic ferromagnets.

2. EXPERIMENTAL RESULTS

The temperature dependence of the magnetic hyperfine interaction was measured by means of the Mössbauer effect on Sn^{119} nuclei with a γ-ray source in the form of the compound $BaSnO_3$, containing Sn^{119m}. The basic measurements were carried out on samples containing 0.5 at.% Sn in a Ni matrix and 0.8% at.% Sn in an Fe matrix (the content of the isotope An^{119} in the tin was equal to 87%). Control measurements were also carried out at certain temperatures with samples containing 0.25 at.% Sn in Ni and 0.15 at.% Sn in Fe; in the limits of achievable accuracy of the measurements ($h(T)$ was determined to within 0.02—0.03), no effect of Sn concentration on the results of the experiment was observed. Inasmuch as the Curie temperature of the investigated samples was rather high, it was assumed in the treatment of the results, that the magnetic field observed at a temperature of 77°K did not differ appreciably from the field at 0°K.

The results of the measurements are shown in Fig. 1. For both alloys, the temperature dependence of the reduced magnetic field $h(T)$ was shown to be stronger than the temperature dependence of the magnetization of the matrices, while in the case of the Fe matrix, the difference between $h(T)$ and $m(T)$ was much greater than in the case of the Ni matrix. As has already been noted, such a great discrepancy cannot be explained by a change in the magnetization of the atoms of the matrix close to the impurity. Moreover, the discrepancies due to this mechanism should be greater

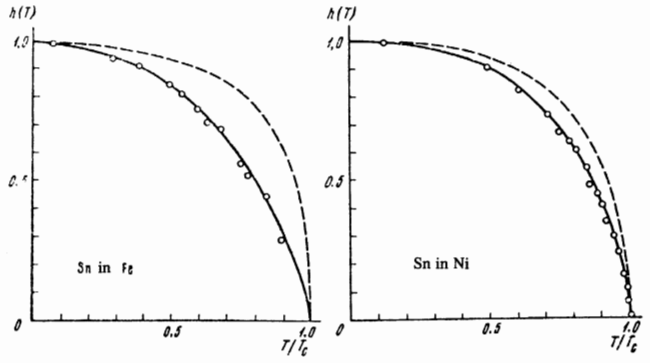

FIG. 1. Temperature dependence of the magnetic field at Sn^{119} impurity atomic nuclei in Fe and Ni matrices. The dashed curve gives the temperature dependence of the magnetization of the matrix, m(T).

in the Ni matrix than in the Fe matrix, inasmuch as the Sn impurity atom strongly damps the magnetic moments of the neighboring atoms in Ni and has only a slight affect in the Fe matrix.[6]

It should be noted that a number of other facts pertaining to the magnetic hyperfine interaction for Sn impurity atoms have not yet received fundamental interpretation. For example, it is known that for Sn atoms in ferromagnetic metallic matrices (in contrast with most other impurity atoms) the magnetic field at the nucleus not only is not proportional to the atomic magnetic moment of the matrix, but in the transition from Fe and Co to Ni even changes sign (H is equal to −83, −22 and +19 kOe, respectively, in the matrices of Fe, Co and Ni). In metallic Cr, a magnetic field of 98 kOe acts on the nuclei of the Sn impurity atoms.[7] This value is greater than the field in the Fe matrix, in spite of the fact that Cr is antiferromagnetic and the atomic moment of Cr is several times smaller than the atomic magnetic moment of Fe.

In the following sections of the paper, we shall show that all these results can be regarded and explained from a single point of view, if we take into account some features of the radial dependence of the exchange interaction, which leads to the appearance of a magnetic field at the nucleus of the impurity atom. Simultaneously, we shall explain why the observed anomalies in the magnetic hyperfine interaction is most strikingly observed for the Sn impurity atoms.

3. QUALITATIVE EXPLANATION OF THE RESULTS

In accordance with the model suggested in[5], the magnetic field at the nucleus of a nonmagnetic impurity atom in a ferromagnetic matrix can be represented in the form of a sum of two large contributions of opposite sign:

$$H = -H^- + H^+. \qquad (1)$$

Both these contributions are connected, in the final analysis, with the polarization of the occupied internal shells of the impurity atom. The positive contribution to the field H^+ is due to the direct interaction of the electrons of the structure with the polarized conduction electrons and is constant for elements of the same period. The negative contribution H^- is a function of the total number (ν) of s-, p- and d-electrons in the external shells of the corresponding free atom. The resulting field is thus the difference of two large contributions and can be positive or negative, depending on the relation between H^- and H^+ which, in turn, depends on ν in known fashion[5].

As is known, for most impurity atoms in homogeneous ferromagnetic matrices (Fe, Co, Ni) the magnetic field at the nucleus is exactly proportional to the atomic magnetic moment μ of the matrix. In the consideration of an isolated impurity in the ferromagnet, the problem as to "local" or "Collective" exchange interactions, leading to the appearance of a field at the nucleus, does not arise. In other words, in this case, in the interpretation of most of the experimental data, it is not important whether the field is determined by the magnetic moments of nearest neighbors of the give atom only, or by the moments of atoms in a large number of coordination spheres. However, this problem arises in the consideration of the magnetic hyperfine interaction for alloys, when atoms with different magnetic moments may be located in different coordination spheres.

Recently, with the help of the Mössbauer effect and NMR, data, have been obtained data on the effect exerted on the magnetic field at a given atomic nucleus of the magnetic moments by the atoms of the matrix, located in different coordinate spheres of the b.c.c. lattice of iron. If part of the Fe atoms is replaced by nonmagnetic atoms (Al, Si, Sn etc.) then additional lines ("satellites") appear in the absorption spectra for Fe^{57}. These lines correspond to a distribution of the nonmagnetic atoms in different coordination spheres close to the given Fe atom.[8-11] An important result of these experiments is the observation of satallites not only at low frequencies (relative to the fundamental line), but also in the high-frequency regions of the spectrum. This means that the appearance of a nonmagnetic vacancy (depending on its position in one coordination sphere or another) can not only decrease but also increase the field at the nucleus of the given atom of Fe. It is well known that the replacement of a single Fe atom by a nonmagnetic atom in the first coordination sphere decreases the magnetic field at the nucleus of the given Fe atom by about 7%;[8-10] consequently, we should conclude (in agreement with the conclusions of the authors of[9,11]) that the increase in the field corresponds to the appearance of a nonmagnetic vacancy in the farther coordination spheres. The field at the nuclei of the Fe atoms in metallic Fe is negative. The considered data show that in metallic Fe the nearest neighbors of a given atom give a negative contribution to the field, since the atoms located in the farther spheres give a positive contribution.

A quantitative estimate of the contributions to the field, corresponding to magnetic moments in different coordination spheres, is complicated by the fact that the data of[8-11] are incomplete and do not agree in detail with one another. If use is made, for example, of the data of[11], then we get a value of +65 kOe for the total contribution to the field by the Fe atoms in spheres III and IV. For Fe atoms, part of the field at the nucleus is due to the characteristic magnetic moment of the atom; however, the effect of the environ-

ment on the value of the field for magnetic and nonmagnetic atoms is qualitatively the same;[12] therefore, it is natural to suppose that for the nonmagnetic impurity atom in the Fe matrix, the radial dependence of the contributions to the field from the vicinity will not differ essentially from the dependence for the Fe atom. For Co and Ni matrices, similar data are lacking; in what follows, we shall assume that the situation for these matrices is qualitatively the same as for the Fe matrix.

For the interpretation of these data on the basis of Eq. (1), we assume that each of the two contributions to the field, H^- and H^+, can be regarded as the sum of partial contributions from the atoms of the matrix, located at different distances from the impurity. The considered experimental data then lead to the conclusion that the ratio between H^- and H^+ for the partial contributions is not constant but depends on the number of the coordination sphere. Even if the total field at the nucleus of the impurity atom is negative ($H^- > H^+$), the atoms of the matrix located sufficiently far from the impurity (for example, in spheres III and IV in accord with the data of[11]) make an additional contribution to the field. It can be shown that the negative contribution is more "local", in a certain sense, than the positive contribution, inasmuch as the latter is totally determined by a large number of coordination spheres.

Now it is not difficult to give a qualitative explanation of these experimental data for Sn impurity atoms, which were listed in Sec. 2. First of all, we consider the fact that the fields observed for the Sn impurity atoms in the Fe, Co and Ni matrices are relatively small. In accord with the model considered in[5], this means that H^- and H^+ for Sn are close together in absolute value and almost compensate one another. Inasmuch as H^- and H^+ are themselves large (about 1000 kOe for Sn in Fe), even a small relative change in the value of one of the contributions has a considerable effect on the field at the nucleus of the Sn atom and can even change the sign of the field. It is now easy to understand the reason for the differences in sign of the field for Sn in Fe and in Ni. The Sn impurity atom in Fe disturbs the neighboring atoms of the matrix almost not at all; therefore, we should assume that the "normal" sign of the field for Sn in metallic ferromagnets is negative. In Ni, the Sn impurity atom strongly perturbs the matrix, giving magnetic moments to the surrounding atoms.[6] Inasmuch as this perturbation falls off with distance, H^- (as a consequence of its greater "locality") decreases more rapidly than H^+; as a result, H^+ becomes dominant and the field at the Sn atom nucleus changes sign. This interpretation is confirmed by the data for Cd, In and Sb impurity atoms, which behave in a fashion similar to Sn in Ni.[6] For these atoms, the "reduced" field H/μ in the Ni matrix is always more positive (for $H > 0$) or more negative (for $H < 0$) than in the Fe matrix.

The large value of the field at the Sn impurity atomic nucleus in Cr is explained in a natural way. The antiferromagnetic orientation of the moments in Cr leads to a strong damping of the field contribution that depends on the more distant neighbors of the impurity atom. Here the field is principally determined by atoms of the coordination sphere I, as a result of which it is large and negative (the sign of the field in the given case is determined by the relative orientation of the moments of the matrix atoms in the first coordination sphere).

Anomalies in the temperature dependence of the magnetic hyperfine interaction for Sn impurity atoms are also the direct consequence of the relative "locality" of the negative contribution to the field. With increase in temperature, the magnetization of the atoms of the matrix located near the impurity falls off more rapidly than the magnetization of the matrix as a whole,[2,3] i.e., the temperature dependence of the mean magnetic moment is different for atoms located at various distances from the impurity. As a consequence of this, the negative contribution to the field depends more strongly on the temperature than the positive one. For example, if the field at low temperatures is small in absolute value and negative, it will fall off rapidly with increase in temperature and for certain conditions can even change sign.

4. TEMPERATURE DEPENDENCE OF THE MAGNETIC FIELD AT Sn IMPURITY ATOMIC NUCLEI IN FERROMAGNETS

We shall consider a simple model which allows us to give not only a qualitative, but also a semi-quantitative explanation of the temperature dependence of the magnetic hyperfine interaction for impurity nonmagnetic atoms. In connection with the fact that data on the radial dependence of the contributions to the magnetic field at the nucleus are still incomplete at the present time even for the Fe matrix, and are not very accurate, we shall consider a limitingly simple form of a model which allows us to restrict ourselves to only a single parameter to be determined. We assume that 1) the negative contribution is completely local, i.e., it is determined only by the atoms of the first coordination sphere, and 2) the positive contribution can be divided into two parts, of which the first, αH^+, is "local" to the same degree as H^-, while the second, $(1 - \alpha)H^+$ is due to the magnetic moments of the atoms of the matrix in the more distant coordination spheres. The parameter $\alpha \leq 1$, which determines the "local" part of the positive contribution to the field, is assumed not to depend on the temperature, but can be different in different matrices. The temperature dependence of the negative contribution can then be represented in the form

$$H^-(T) = H^-(0)K(T)m(T), \qquad (2)$$

where $K(T) \leq 1$ is a function characterizing the decrease in the mean magnetization of the atoms of the matrix near the impurity, in comparison with $m(T)$. Unfortunately, there are no experimental data which would permit us to determine this function directly; in what follows, we have used the function $K(T)$ determined as the result of a theoretical calculation of Lovesey and Marshall[2]. For the "local" part of H^+, the temperature dependence will be the same as for H^-; the temperature dependence for the "nonlocal" part of H^+ is assumed to be identical with $m(T)$. Therefore, for the positive contribution

$$H^+(T) = \alpha H^+(0) K(T) m(T) + (1-\alpha) H^+(0) m(T). \quad (3)$$

Formulas (1)—(3) lead to the following result for the temperature dependence of the magnetic field at the impurity atom nucleus:

$$h(T) = \frac{m(T)}{1-\gamma} \{K(T)(1-\alpha\gamma) - \gamma(1-\alpha)\}, \quad (4)$$

where $\gamma = H^+(0)/H^-(0)$. For the analysis of the experimental data, it is convenient to consider the difference between the matrix magnetization and the magnetic field:

$$\Delta(T) = m(T) - h(T) = m(T) \frac{(1-\alpha\gamma)(1-K(T))}{1-\gamma}. \quad (5)$$

Analysis of this expression shows that Δ can be (depending on the relation between the parameters α and γ) positive or negative, while the maximum discrepancy between h(T) and m(T) is observed (in correspondence with the qualitative consideration given in Sec. 3) for γ close to unity.

The parameter γ can be determined with sufficient accuracy with the help of an empirical formula for the field, obtained previously in[5]. For our analysis it is convenient to rewrite this formula in the form

$$H = \mu Z_0^{1/3} [5.0 - \nu(1.6 - 0.09\nu)], \quad (6)$$

where Z_0 is the number of electrons in the filled shells of the impurity atom, ν the number of electrons in the outer shells of the corresponding free atom. (The coefficients of Eq. (6) were determined with account of new experimental data on the fields at the impurity atom nuclei in the Fe matrix; therefore, they differ somewhat from the coefficients given earlier in[5].) In accord with Eq. (6), $H^+ = 5.0\ \mu Z_0^{1/3}$; For Sn in the Fe matrix, we find $\gamma = 0.94$. The empirical formula (6) allows us to determine H^+ with an accuracy to within 10%; however, this uncertainty does not introduce a significant error in the parameter γ, inasmuch as the experimental value of the field at the nucleus is known to within about 2%.

The parameter α can be found from a comparison of the measured function $\Delta(T)$ with the formula (5). Taking into account the approximate character of the considered model, it would be desirable to obtain an estimate of this parameter by an independent method. For the Fe matrix, the approximate value of α can be determined by using the NMR data of Mendis and Anderson considered above[11] and Eq. (6) (for the calculation of the total value of the positive contribution); these data give the value $\alpha = 0.87$ for the Fe matrix. For the Ni matrix, the value of α can be estimated by a more indirect method. With this purpose, we compared the experimental data on the fields at the impurity atomic nuclei Cd, In, Sn, and Sb (see Sec. 3) in Fe and Ni matrices, assuming that the Fe matrix is not disturbed by the impurity atom, and the weakening of the negative contribution to the Ni matrix is proportional to the decrease in the moments of the matrix atoms in the first coordination sphere (the corresponding data were obtained with the help of neutron scattering.[6]) Data for all four impurity atoms gave close values for the parameter α, lying in the range 0.5—0.6. The decrease in the parameter α for Ni (in comparison with Fe) corresponds to a decrease

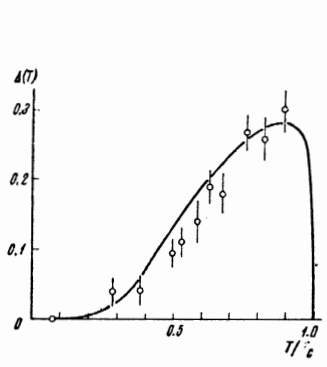

FIG. 2

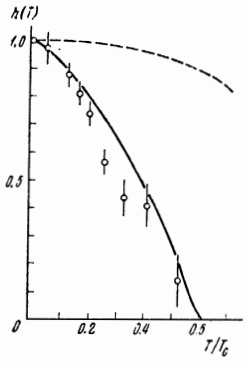

FIG. 3

FIG. 2. Dependence $\Delta(T) = m(T) - h(T)$ for Sn^{119} impurity atoms in the Fe matrix. The solid curve was computed from Eq. (5) for the parametric values $\gamma = 0.94$, $\alpha = 0.8$.

FIG. 3. Temperature dependence of the magnetic field at the nuclei of Sn^{119} impurity atoms in a f.c.c. Co matrix. The experimental data were obtained from [4]. The solid curve was computed from Eq. (4) for the parametric values $\gamma = 0.98$, $\alpha = 0.6$. The dashed curve gives the temperature dependence of the magnetization of the matrix, m(T).

in the "local" part of H^+ as a consequence of the perturbation of the matrix by the impurity atom, and also possibly reflects the difference in the electron structure of the matrices.

Figure 2 shows the comparison of the function $\Delta(T)$ found experimentally for Sn in Fe with the result of calculation from Eq. (5). It is seen that it is possible to describe the results of the experiments quite satisfactorily by means of Eq. (5). It is important here that, in spite of the approximate character of the model considered, excellent agreement with experiment is achieved for the values of the parameter α close to that obtained above from other data.

It is seen from the results shown in Fig. 1 that for Sn in Ni, the discrepancy between h(T) and m(T) is much less than for Sn in Fe. Within the framework of the considered model, this fact is a consequence of the damping of the moments of the atoms of Ne near the impurity, which leads to an increase in the relative role of the "nonlocal" part of the positive contribution. However, quantitative agreement of Eq. (5) with the measured function $\Delta(T)$ for Sn in Ni has not been achieved. For $\gamma > 1$ and $\alpha \sim 0.6$, Eq. (5) leads to negative values of $\Delta(T)$, since $\Delta(T)$ actually remains positive. This lack of correspondence can be explained, however. According to the data of Comly, Holden and Low,[6] the impurity atom of Sn in the Ni matrix suppresses the moments of the atoms of the matrix, not only in the first coordination sphere, but (although to a lesser extent) also in the further spheres. Here the temperature dependence of the "nonlocal" part of H^+ no longer follows m(T) accurately, but falls off somewhat more rapidly. This situation can be considered formally by introduction of the corresponding corrections in Eq. (3); however, such a complication of the model is scarcely justified at the present time, since the temperature dependence of the mean magnetization of the atoms in the different coordination spheres of the Ni matrix cannot be found from experimental data.

In conclusion, we apply the considered model to the

interpretation of the very great discrepancies between h(T) and m(T) for Sn in the Co matrix, which were observed by Jain and Cranshaw.[4] The large discrepancies in this case are due to the fact that H(0) is negative and very small in absolute value ($\gamma = 0.98$). Unfortunately, data on neutron studies are lacking for Co, from which one could determine the character of the effect of the impurity on the matrix and estimate the parameter α. As is seen from Fig. 3, excellent agreement of the results of the calculation from Eq. (4) with the experimental data is achieved for a value of the parameter α close to the estimate obtained for the Ni matrix. It should be noted that, in accord with our interpretation, the field at the nucleus of the Sn impurity atom in the Co should change sign at sufficiently high temperatures. However, the corresponding measurements are difficult, as the result of the extremely low solubility of Sn in Co.

The considered anomalies in the temperature dependence of the magnetic hyperfine interaction should, of course, be observable for other impurity atoms. Here, however, the accuracy of the measurements ought to be much higher, inasmuch as the discrepancies between h(T) and m(T) fall off rapidly, both with increase and decrease of the parameter γ. Great interest attaches to the study of H(T) for Sn in ordered alloys, for which atoms with strongly different magnetic moments are located in different coordination spheres. The model assumed in the present work can be refined when more complete data are obtained on the effect on the magnetic hyperfine interaction of the atoms located in different coordination spheres in metallic ferromagnetic matrices.

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Note added in proof (3 November, 1969). Recently, we learned of new results of the study of the magnetic hyperfine interaction for Sn^{119} impurity atoms. In the work of Cranshaw (T. E. Cranshaw, J. Appl. Phys. 40, 1481 (1969), the measurements of h(t) are continued for Sn^{119} in f.c.c. Co in the region of high temperatures (up to 1273°K). It is shown that for temperatures exceeding 800°K, the field actually changes sign; the observed dependence of the field on the temperature is in excellent agreement with that calculated from Eq. (4). The temperature dependences of the magnetic field for Sn^{119} in Fe and Ni were measured by Huffman, Schwerer and Dunmyre (G. P. Huffman, F. C. Schwerer and G. R. Dunmyre, J. Appl. Phys. 40, 1487 (1969); the results of the measurements agree with the experimental results of our work. However, the interpretation of the experimental data, based on a consideration of the spans of the wave functions of the 3d- and 5s-electrons (in the work of Cranshaw) or the mechanism of Lovesey and Marshall [2] (in the work of Huffman et al.) does not permit, in our opinion, an explanation from a single viewpoint of all the experimental data on the magnetic hyperfine interaction for Sn^{119} impurity atoms in metallic ferromagnets.

[1] V. Jaccarino, L. R. Walker, and G. K. Wertheim, Phys. Rev. Lett. 13, 752 (1964); G. G. Low, Phys. Lett. 21, 497 (1966); D. A. Shirley, S. S. Rosenblum and E. Matthias, Phys. Rev. 170, 363 (1968).

[2] S. W. Lovesey and W. Marshall, Proc. Phys. Soc. (London) 89, 613 (1966).

[3] H. P. van de Braak and W. J. Caspers, Z. Physik 200, 270 (1967).

[4] A. P. Jain and T. E. Cranshaw, Phys. Lett. 25A, 421 (1967).

[5] A. E. Balabanov and N. N. Delyagin, Zh. Eksp. Teor. Fiz. 54, 1402 (1968) [Sov. Phys.-JETP 27, 752 (1968)].

[6] J. B. Comly, T. M. Holden and G. G. Low, Proc. Phys. Soc. (London) 1C, 458 (1968); G. G. Low, J. Appl. Phys. 39, 1174 (1968).

[7] R. Street, B. C. Munday, B. Window and I. R. Williams, J. Appl. Phys. 39, 1050 (1968).

[8] M. B. Stearns, Phys. Rev. 147, 439 (1966).

[9] T. E. Cranshaw, C. E. Johnson and M. S. Ridout, Phys. Lett. 21, 481 (1966).

[10] J. J. Murphy, J. I. Budnick and S. Skalski, J. Appl. Phys. 39, 1239 (1968);

[11] E. F. Mendis and L. W. Anderson, Phys. Rev. Lett. 19, 1434 (1967).

[12] A. E. Balabanov, N. N. Delyagin, A. L. Erzinskyan, V. P. Parfenova and V. S. Shpinel', Zh. Eksp. Teor. Fiz. 55, 2136 (1968); [Sov. Phys.-JETP 28, 1131 (1969)].

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