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Interaction Between the *d* Shells in the Transition Metals*

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It is assumed (1) that the interaction between the incomplete *d* shells of the transition elements is insufficient to disrupt the coupling between the *d* electrons in the same shells, and (2) that the exchange interaction between adjacent *d* shells always has the same sign irrespective of distance of separation. The direct interaction between adjacent *d* shells then invariably leads to a tendency for an antiferromagnetic alignment of *d* spins. The body-centered cubic structure of the transition metals V, Cr, Cb, Mo, Ta, and W is thereby interpreted, as well as more complex lattices of certain alloys. It is demonstrated that the spin coupling between the incomplete *d* shells and the conduction electrons leads to a tendency for a ferromagnetic alignment of *d* spins. The occurrence of ferromagnetism is thereby interpreted in a much more straightforward manner than through the *ad hoc* assumption of a reversal in sign of the exchange integral. The occurrence of antiferromagnetism and of ferromagnetism in various systems is readily understood, and certain simple rules are deduced for deciding which type of magnetism will occur in particular alloys.

I. INTRODUCTION

A REVIEW of the crystal structure and of the magnetism of the transition elements has led the author to very simple principles which appear to govern the interaction between the incomplete *d* shells of neighboring atoms.

The first principle is that, at least in the fourth column (V, Cb, Ta) and beyond, the spin correlation between the electrons in the incomplete *d* shell of a single atom is essentially the same when the atom forms part of a solid as when it is isolated in the gaseous state. In the isolated atom the lowest energy state is given by that electron configuration in which the incomplete *d* shell has the highest net electron spin, i.e., in which all unpaired electrons have spins pointing in the same direction. As has been shown by Slater,[1] the physical basis for this rule of highest net electron spin is that electrons with similar spin automatically avoid close proximity. According to this first principle the incomplete *d* shell of an atom in a metal also has the highest net electron spin consistent with the number of electrons therein.

The second principle is that the exchange integral between *d* shells of adjacent atoms has always the same sign as in the H_2 molecule. The direct interaction between *d* shells of adjacent atoms is thus of such a sign as tends, in all circumstances, to lead to an antiferromagnetic configuration of the *d* shell spins. This principle is contradictory to the usual *ad hoc* assumption that within a certain range of the ratio (radius of *d* shell/closest distance of approach) the exchange integral is of reversed sign.

The third principle is that the spin of an incomplete *d* shell is strongly coupled to the spin of the conduction electrons. This coupling tends to align the spins of the incomplete *d* shells in a ferromagnetic manner. It is only when this indirect coupling dominates over the direct coupling between adjacent *d* shells that ferromagnetism is possible.

In the present paper no attempt will be made to deduce these principles from theory. As has been pointed out by Hartree,[2] the electron distribution in the outer regions of the *d* shells is extremely sensitive to small changes in the potential. A theoretical deduction of the interaction between *d* shells will therefore be very difficult. The purpose of the present paper is to point out the many diverse observations of structure and of magnetic properties which may be correlated by these three principles. They will, however, be supported by considerations of orders of magnitude.

The physical basis for the first principle, the retention of the spin coupling of the electrons in an incomplete *d* shell, must reside in the large magnitude of this coupling compared with the band width of the *d* shell. In Cr 2.5 ev (58,000 cal/mole) are required to reverse the spins of two of the five electrons in the 3*d* shell.[3] This coupling is smaller than the computed *d* band width in[4] Fe and in[5] W. However, when similar computations are carried out by the Hartree-Fock method under the assumption of highest net electron spin, the computed radius of the *d* shell must automatically contract, for the correlations thereby introduced will allow the *d* electrons to come closer to the nucleus without at the same time coming closer to one another. Such a contraction in radius will of course lower the computed band width.

The second principle has a purely empirical basis. Heisenberg[6] and others have demonstrated that it is not unreasonable to expect the exchange integral to reverse sign as the quantum number increases. However, in no cases other than in the ferromagnetism of the metals in the first transition period have effects been observed which are attributable to a reversal in the sign of this integral. Not even an attempt at a theoretical justi-

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[1] J. C. Slater, Phys. Rev. 34, 1293 (1929).

[2] D. R. Hartree, Proc. Roy. Soc. 141, 282 (1950).

[3] R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932).

[4] J. C. Slater, Phys. Rev. 49, 537 (1936).

[5] M. F. Manning and M. I. Chodorow, Phys. Rev. 56, 787 (1939).

[6] W. Heisenberg, Z. Physik 49, 619 (1928).

TABLE I. Correlation of binding energy with electronic structure of isolated atoms.

Ni($3d^84s^2$) 98,000*	Cu($3d^{10}4s$) 82,000	Zn($3d^{10}4s^2$) 31,000
Pd($4d^{10}$)	Ag($4d^{10}5s$) 69,000	Cd($4d^{10}5s^2$) 27,000
Pt($5d^96s$) 125,000	Au($5d^{10}6s$) 91,000	Hg($5d^{10}6s^2$) 14,000

* Latent heat of vaporization in cal/mole.

fication can be given for the usual assumption for a reversal in sign restricted to a given range of atomic separation. The persistence of this concept of a reversal in the sign of the exchange integral is a consequence solely of the absence of a better theory of ferromagnetism.

The third principle is based upon a firm foundation. In the isolated atoms a single electron in the outer *s* shell is always coupled fairly strongly to the spin of the inner incomplete *d* shell, the lowest energy always corresponding to the spin of the *s* electron being parallel to that of the *d* shell. Thus in the first transition group this coupling varies from a maximum of 0.93 ev for Mn to a minimum[3] of 0.39 ev for Ni. This coupling is proportional to the density of the *s* electron in that region of the atom where the radial charge density of the *d* electrons is a maximum. Now in the isolated atom the outer *s* electron spends only about one-third of its time within the radius r_s associated with the atomic volume in the condensed state. As the atoms condense from a gaseous to a metallic state the *s* electrons will therefore increase by about a factor of three the time spent in the vicinity of the *d* electrons, and hence their coupling with these electrons will be increased by the same factor.

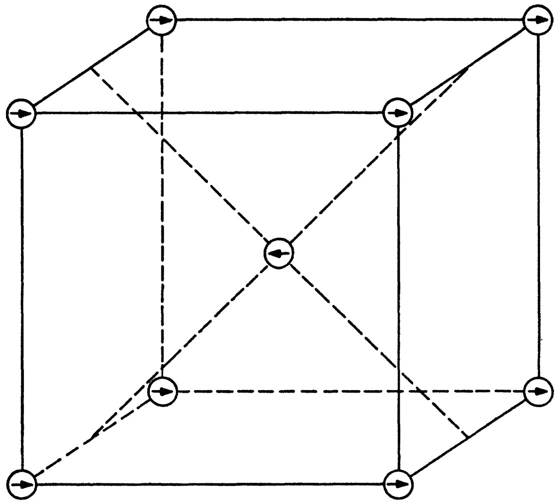

FIG. 1. Postulated antiferromagnetic spin arrangement in V, Cr, Cb, Mo, Ta, W.

TABLE II. Crystal structure of the transition metals.

Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
fcc hcp	fcc hcp	bcc hcp	bcc	bcc	4 types	fcc bcc	fcc hcp	fcc
Cr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd
fcc	hcp	bcc hcp	bcc	bcc	*	hcp	fcc	fcc
Yb	Lu	Hf	Ta	W	Re	Os	Is	Pt
*	hcp	hcp	bcc	bcc	hcp	hcp	fcc	fcc

* Structure unknown.

II. CRYSTAL STRUCTURE

According to the first two principles, the direct exchange interaction tends to align the spins of the incomplete *d* shell in an antiferromagnetic manner, and this tendency will be stronger the larger the spin of the *d* shells. A rough but not exact correlation exists between the magnitude of the spins of the *d* shell of an atom in the isolated gaseous state and in the condensed solid state. Some transition atoms have two outer *s* electrons when isolated. We can be quite sure from the data in Table I that two electrons will not stay in the outer shell when these atoms are condensed. The great drop in the heat of vaporization in passing from Cu to Zn, from Ag to Cd, and from Au to Hg is due primarily to the inability of the second *s* electron in the latter atoms to be demoted to an inner *d* shell and thereby avoid the necessity of acquiring the large Fermi kinetic energy associated with the second conduction electron per atom. If we tentatively assume that one electron remains in the outer *s* state, or more correctly in the conduction band, we find that Cr, Mo, and W will have 5 electrons in the incomplete *d* shell. This is just the number which will give the greatest *d* shell spin. Hence of all the transition elements, Cr, Mo, and W will have the greatest tendency to form a lattice structure in which all nearest neighbors have anti-parallel spins. The most common crystal lattices of the elements are fcc (face-centered cubic) and hcp (hexagonal close-packed). No arrangement of spins on these two types of lattices can satisfy the requirement that all nearest neighbors have antiparallel spins, for some of the nearest neighbors of a particular atom are nearest neighbors of one another. As may be seen in Fig. 1 this requirement is, however, satisfied by the bcc (body-centered cubic) lattice in which Cr, Mo, and W do in fact crystallize. While W may be obtained by electrolysis in another modification, this element has no stable allotropic modification.

From the value of the saturation magnetization in Fe, Co, and Ni it is commonly accepted that the conduction band has less than one electron per atom, the precise number being 0.2, 0.7, 0.6 for the above three elements, respectively. If we generalize these findings and assume that the number of electrons in the conduction band is always less than unity for the transition metals, we arrive at the conclusion that next to Cr, Mo, and W the transition elements which have the greatest number of unpaired electrons are V, Cb, and Ta. The observation that these three metals likewise crystallize in the bcc lattice, with no stable allotropic form, is a strong vindication of our postulated principles. No transition metals other than these six are stable only in the bcc lattice. As seen from Table II, Ti, Zr, and Fe also exist as bcc lattices, but they have other stable modifications.

The unstable modification of W, formed by electrolysis, has the structure illustrated in Fig. 2. Here one-fourth of the atoms, those occupying the bcc lattice positions, have no close neighbors. The remaining W atoms are closely packed along linear rows. Exchange repulsion within these rows is presumably avoided by the spins of the *d* shells alternating in sign. This same lattice type, A15, has been found elsewhere only in $\mathrm{V_3Si}$ and in $\mathrm{Cr_3Si}$.* In these silicides the Si atoms occupy the bcc lattice positions, while the V and Cr atoms occur only in the close packed rows. The limitation of the A15 structure to the transition elements in the fourth and fifth columns is again a strong confirmation of our postulated principles.

Many ordered *d* spin arrangements will at least partially minimize the exchange repulsion between the *d* shells. Thus suppose that alternate (001) planes in a fcc lattice had *d* shell spins of alternating direction, as illustrated in Fig. 3. Then each *d* shell would have a full repulsive interaction with only four of its twelve nearest neighbors, leading to a lower energy than given by a random distribution of spin. Since the exchange repulsion will be between nearest neighbors in the same (001) plane, the ordered spin arrangement postulated in Fig. 3 would lead to a tetragonal lattice, the c/a ratio being less than unity. The γ-phase of Mn has all the earmarks of being such an ordered phase. As quenched its structure is face-centered tetragonal, with a c/a ratio of 0.94. Since the high temperature γ-phase is very difficult to retain in pure manganese, investigations are usually carried out with deliberate additions of some impurity, such as Cu. Worrell[7] has found that such alloys (containing about 12 percent Cu) when quenched have a microstructure apparently consisting of finely spaced twins. A similar twin-like microstructure has later been reported[8] in quenched Mn with additions of Cr. The author[9] has interpreted this structure as indicating that at the higher temperature the lattice was cubic, and became tetragonal only on cooling. Due to the constraints of neighboring grains, a given grain can become tetragonal only if it becomes heavily twinned. Only in this manner can the grains avoid a large free energy of elastic strain.

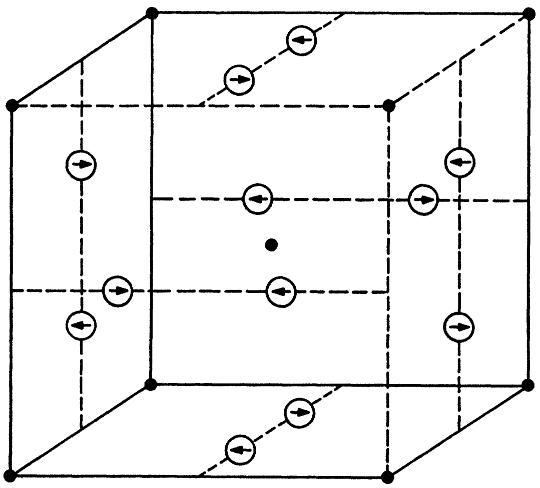

FIG. 2. Postulated antiferromagnetic spin arrangement in $\mathrm{V_3Si}$, $\mathrm{Cr_3Si}$: ● silicon atom. ○ transition metal atom.

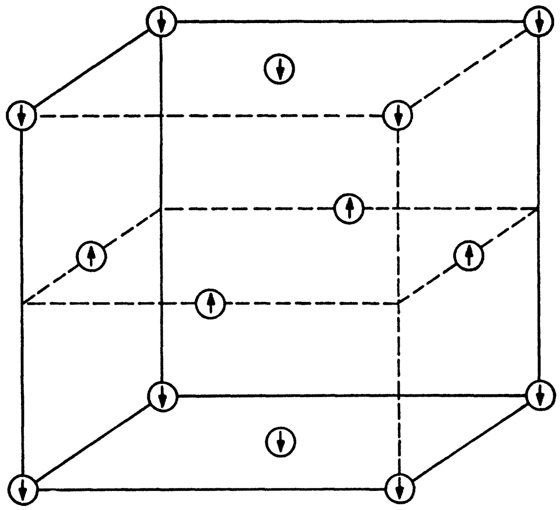

FIG. 3. Postulated antiferromagnetic spin arrangement in fct Mn.

III. MAGNETIC PROPERTIES

According to the principles postulated in the present paper, three types of spin coupling govern the magnetic properties of the transition metals. The relative magnitudes of these three types of coupling in a particular metal determine the type of its magnetic behavior.

The first coupling arises from the direct exchange between the incomplete *d* shells of nearest neighbors. If we are interested in the variation of this exchange energy only with the degree of ordering of the net spins of the *d* shells, we may represent this energy as $\frac{1}{2}\alpha S_d^2$ per atom. Here S_d is the mean component per atom, in units of Bohr magnetons, of the net spin of the *d* shells along the direction of magnetization. As discussed in the introduction, we postulate that α is positive in all circumstances. Its magnitude will, however, decrease

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* *Note added in proof:* A further example of the A15 structure is $\mathrm{Mo_3Si}$ (Templeton and Dauben, Acta Cryst. **3**, 261 (1950)).

[7] F. T. Worrell, J. Appl. Phys. **19**, 929 (1948).

[8] Carlile, Christian, and Hume-Rothery, J. Inst. Metals **76**, 169 (1949).

[9] C. Zener, *Elasticity and Anelasticity of Metals* (University of Chicago Press, Chicago, 1948), pp. 160–163.

rapidly with a decreasing amount of overlap of the *d* shells of adjacent atoms. Its magnitude will therefore be smallest for those elements in the upper right corner of Table II.

The second spin coupling arises from the exchange between the conduction electrons and the inner *d* electrons. This coupling energy we may represent as $-\beta S_d S_c$ per atom. Here S_c is the net magnetization of the conduction electrons, expressed in units of Bohr magnetons per atom. The coefficient β is always positive. In the introduction we have seen that the value of β can be estimated from spectroscopic data of the isolated atoms, and is of the order of magnitude of one electron volt.

The third spin coupling arises from the Fermi kinetic energy of the conduction electrons. This kinetic energy is a minimum when the same number of conduction electrons have spins pointing along as pointing against the direction of magnetization. Under these conditions S_c is zero. Since the increase in Fermi kinetic energy associated with an unbalanced distribution of the conduction electrons must be an even function of S_c, we may represent this increase in kinetic energy by $\frac{1}{2}\gamma S_c^2$ per atom provided the inbalance is small. The coefficient γ may be expressed in terms of the kinetic energy at the top of the Fermi distribution ϵ, and in terms of the number of conduction electrons per atom, n. This relation is

$$\gamma = 2\epsilon/3n.$$

The magnitude of γ is several electron volts.

Upon combining the above three types of spin coupling, we obtain for the spin energy

$$E_{\mathrm{spin}} = \tfrac{1}{2}\alpha S_d^2 - \beta S_d S_c + \tfrac{1}{2}\gamma S_c^2. \tag{1}$$

Since the contribution of the conduction electrons to the entropy of the system is negligible, the equilibrium value of S_c is that which minimizes E_{spin}. We thereby obtain

$$S_c = (\beta/\gamma)S_c. \tag{2}$$

We thus anticipate that S_c has a value of several tenths.

Upon inserting (2) into (1) we find

$$E_{\mathrm{spin}} = \tfrac{1}{2}\{\alpha - (\beta^2/\gamma)\}S_d^2. \tag{3}$$

The coefficient $\{\alpha - \beta^2/\gamma\}$ thus corresponds to the "inner field" of Weiss. The formal theory of ferromagnetism may thus be based upon the present postulated principles as well as upon the more conventional concepts which also lead to an inner field. The type of magnetic behavior will be determined solely by the relative magnitudes of β^2 and $\alpha\gamma$. Thus

$$\beta^2 \gtrless \alpha\gamma \text{ for } \begin{matrix}\text{ferromagnetism}\\ \text{antiferromagnetism.}\end{matrix} \tag{4}$$

Since it is not the purpose of the present paper to develop the quantitative theory of ferromagnetism, it will be sufficient to note that the ferromagnetic coupling term $\frac{1}{2}(\beta^2/\gamma)S_d^2$ is of the right order of magnitude. From the above estimates we deduce that this coupling energy is of the order of magnitude of a tenth of an ev per atom while the observed magnetization energies of Fe, Co, and Ni are 0.07, 0.05, and 0.01 ev per atom, respectively.

The value of our theory in its present qualitative stage lies in its simple interpretation of the various observed types of magnetic properties without the aid of *ad hoc* hypotheses, and of its power in predicting the magnetic properties of systems as yet not investigated. Ferromagnetism will be observed in all systems for which the first inequality of (4) is satisfied, i.e., in which the neighboring incomplete *d* shells are sufficiently far apart so that the indirect ferromagnetic coupling through the conduction electrons dominates over the direct antiferromagnetic coupling. Among the pure transition metals this condition is most likely to occur in the last elements of the first transition group. An interesting possibility occurs in alloys. Suppose we have a material in which transition atoms are dissolved in a metal or alloy otherwise containing only completed inner shells, and that the transition atoms have ordered positions such that they are not nearest neighbors of one another. In such an alloy there would be no direct exchange between incomplete *d* shells. The ferromagnetic coupling via the conduction electron must, therefore, give rise to ferromagnetism at a sufficiently low temperature. The Heusler alloys are one example of the above postulated structure. Here the transition atoms, namely, Mn, occupy ordered positions which are next next nearest neighbors of one another.[10] The other constitutents of the Heusler alloys have only completed inner shells. The ferromagnetism of the Heusler alloys disappears upon disordering.[11] While in the ordered lattice no Mn atom has another Mn atom as nearest neighbor, or even as a next nearest neighbor, in the disordered bcc lattice each Mn atom has on the average two other Mn atoms as nearest neighbors. The resulting direct exchange coupling must, therefore, considerably reduce the ferromagnetic Curie temperature.

A large distance of separation between incomplete *d* shells insures ferromagnetic behavior only when conduction electrons are present to provide the necessary ferromagnetic coupling. In $MnCl_2$ the neighboring Mn ions are comparatively far apart, 40 percent further than in metallic Mn. $MnCl_2$ does not, however, have any conduction electrons. The small direct exchange, therefore, gives rise to the observed antiferromagnetism. The Mn ions occur in linear chains, so the antiferromagnetic structure may be obtained simply by alter-

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[10] C. S. Barrett, *Structure of Metals* (McGraw-Hill Book Company, Inc., New York, 1943), p. 234.

[11] The author is indebted to Professor C. S. Smith for this observation.

nating spins along the chains,[12] just as in the case of V_3Si, Cr_3Si and in the β-phase of *W*.

The antiferromagnetic direct coupling between *d* shells, and the ferromagnetic indirect coupling via the conduction electrons, are not the only possible types of spin coupling between the incomplete *d* shells. Another indirect spin coupling, called superexchange, is possible through intervening nonmagnetic atoms. This coupling has recently been discussed in full by Anderson.[13]

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[12] The author is indebted to Professor W. Stout for this observation.

[13] P. W. Anderson, Phys. Rev. **79**, 350 and 705 (1950).

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Pressure Dependence of Second Sound Velocity in Liquid Helium. II*

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The velocity of second sound as a function of pressure and temperature has been measured to 0.95°K by a pulse method. The quantitative dependence of the rise in velocity upon pressure is found to support the role of the phonons in contributing to the normal fluid flow alone.

I. INTRODUCTION

THE properties of liquid He II have been explained most satisfactorily by the "two fluid" concept advanced in the theories of Tisza[1] and Landau.[2] Each theory regarded liquid helium as composed of a "normal fluid" fraction and a "superfluid" fraction, although the origin of these two fluids was assigned to different molecular mechanisms. In the temperature range just below the lambda-point Tisza, following the suggestion of London, considered the transverse excitations to be similar to those of a Bose-Einstein gas, appropriately modified by the liquid state. Experiments showing no superfluidity in He^3 have borne out this view, as opposed to the roton model of Landau. On the other hand, Landau considered the longitudinal excitations, the Debye phonons, as a component of the normal fluid flow only, rather than as associated with the fluid as a whole, which was Tisza's view. The phonons are masked by the Bose-Einstein excitations at higher temperatures, but below about 1.1°K their effect is evident. The rise in second sound velocity [3–5] at low temperature and the sustained existence of the waves without undue attenuation tends to bear out the hypothesis that the new type of excitation predominant below 1°K is associated with the normal fluid flow only, and not with the superfluid. The present experiment takes advantage of the large pressure dependence of first sound velocity in liquid helium to investigate whether this low temperature excitation is indeed a phonon effect.

II. EXPERIMENT

Second sound is a type of wave motion most easily excited by the heating of liquid helium. Pellam has developed a pulse method [4,6] which was used by the authors to measure the velocity to below 1°K at vapor pressure.[3] Peshkov has created standing waves to determine the velocity at vapor pressure[5] down to 1° and at higher pressures[7] down to 1.3°.

A pulse method of exciting second sound similar to that formerly used in this work[3,6] was employed again. The chief innovation was the installation of a delay line in the timing mechanism. This permitted a view of the pulse on a faster, continuous sweep and hence a more accurate determination of its leading edge. A DuMont 246 oscillograph was used to trigger the pulse generator and to actuate the delay line. The pulse generator excited the carbon resistor of the second sound chamber. Another carbon resistor, acting as a resistance thermometer, received the second sound pulse, which was amplified and fed into the vertical deflection plates of a second 246D oscillograph. This last oscillograph was triggered by the delay line. The movable marker of the receiver oscillograph could be adjusted on the sweep so that it coincided with the edge of the pulse. By reading the marker dial and by knowing the delay, one could obtain the transit time for the pulse. The capacitative pick-up within the Dewar from the transmitting pulse could be amplified easily to give a sharp leading edge when viewed on the final oscillograph. In doing this, we could not detect any instrumental delay caused by the timing system.

The second sound chamber itself was sealed with solder for immersion in a liquid helium bath. Inside the chamber a thin sleeve separated the carbon resistors and determined the fixed path of 4.23 cm. Four capillaries with an inner diameter of 0.020 in. led to the chamber. Two of these acted as electrical shields for the wires while the other two were pressure lines, one to

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[1] L. Tisza, Phys. Rev. **72**, 838 (1947).

[2] L. Landau, J. Phys. USSR **5**, 71 (1941).

[3] R. D. Maurer and M. A. Herlin, Phys. Rev. **76**, 948 (1949).

[4] J. R. Pellam and R. B. Scott, Phys. Rev. **76**, 869 (1949).

[5] V. Peshkov, J. Phys. USSR **10**, 389 (1946); JETP USSR **18**, 1951 (1948).

[6] J. R. Pellam, Phys. Rev. **75**, 1183 (1949).

[7] V. Peshkov and K. N. Zinovyeva, JETP USSR **18**, 438 (1948).