PHYSICAL REVIEW B VOLUME 14, NUMBER 8 15 OCTOBER 1976

Questions about the Mayer–El Naby optical anomaly in potassium*

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(Received 19 January 1976)

The large, optical-absorption anomaly in the reflection spectrum of potassium, discovered by Mayer and El Naby has a threshold near 0.6 eV and maximum near 0.8 eV. The failure of other workers to reproduce this effect has led to a premature conclusion that it was an experimental artifact. The recent discovery by Harms of how to reproduce it in a controlled way reestablishes the need for a satisfactory explanation. Since the anomaly is turned on by the presence of a KOH surface layer, we report transmission measurements on KOH between 0.5 and 1.1 eV. These show that absorption in KOH cannot be the cause. A number of other extrinsic mechanisms are also considered. Finally we entertain the possibility that the absorption is intrinsic to the metal. This would require potassium to be optically anisotropic. If the direction of the optic axis is influenced by the presence of the KOH layer, a quantitative account of the diverse observations is possible. Two critical experiments are proposed which may distinguish intrinsic and extrinsic mechanisms.

I. INTRODUCTION

The purpose of this paper is to revitalize interest in the problem of the origin of the Mayer–El Naby optical-absorption anomaly,[1] observed in the near-infrared reflection spectrum of potassium. Study of this enigma has subsided since its discovery in 1963 because other workers[2-4] were unable to reproduce it. The conventional view is that the original anomaly was spurious or, at least, unrelated to the properties of potassium.

Recently, Harms,[5] in an extensive study, has shown that the Mayer–El Naby anomaly can be reproduced at will in a controlled way. Freshly prepared (bulk) metal-vacuum surfaces can be obtained which show no trace of the absorption anomaly (see curve *A* of Fig. 1). Curves *B*, *C*, *D*, and *E* were obtained after successive introduction of small amounts of H_2O vapor into the vacuum chamber, otherwise kept at $\sim 10^{-10}$ Torr. The dashed curve *M* is one obtained by Mayer and El Naby.[1] The chemical reaction between potassium and trace amounts of H_2O is

$$K + H_2O \rightarrow KOH + \tfrac{1}{2}H_2. \qquad (1)$$

Consequently, we conclude that curves *B*, *C*, *M*, *D*, and *E* are the absorption spectra of potassium surfaces having increasing amounts of KOH on the surface.

The problem, of course, is to account for the magnitude and spectral shape of the absorption shown in Fig. 1. The absorption threshold is near 0.6 eV, the peak is near 0.8 eV, and the asymmetric high-energy tail extends beyond the 1.3-eV threshold for interband absorption in potassium. When present, the anomalous absorption is an order of magnitude larger than the observed[3,4] interband absorption. (The data shown were obtained by reflection measurements of *p*- and *s*-polarized light having a 75° angle of incidence, and interpreted by employing the Fresnel equations.[6])

II. EXTRINSIC MECHANISMS

Since the anomalous loss of reflectivity near 0.8 eV is associated with the presence of KOH

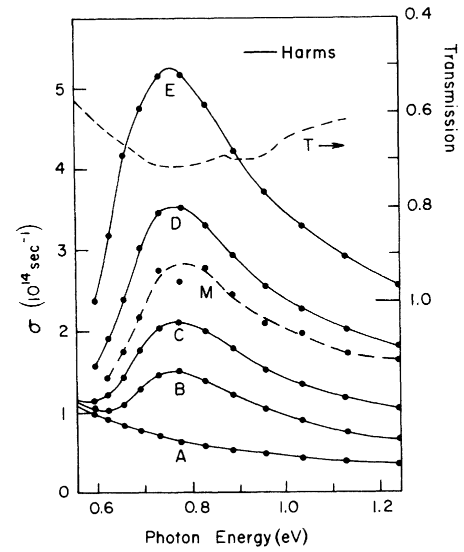

FIG. 1. Curve *A* is the optical conductivity (absorption) at a clean bulk-potassium–vacuum interface. Curves *B*, *C*, *D*, and *E* were obtained on the same specimen after successive exposure to trace amounts of H_2O. These data are from Harms, Ref. 5. The dashed curve *M* is one obtained by Mayer and El Naby, Ref. 1. The dashed curve *T* is an inverted plot of the transmission through 0.01 cm of KOH sandwiched between glass slides. All data are at room temperature.

on the potassium surface, it is natural to assume that this (apparent) absorption peak has an extrinsic origin, not associated with the fundamental optical properties of bulk potassium. Such a conclusion is not warranted, however, until a physical mechanism can be suggested which accounts for the experimental observations qualitatively. We consider below a number of possibilities.

A. Absorption in KOH

KOH is a transparent insulator and would not be expected to absorb in the near infrared. The spectral region of interest is between $h\nu = 0.5$ and 1.1 eV. Infrared data for $h\nu < 0.5$ eV can be found,[7] but we have not located any for the relevant energy. We therefore report our own observations of the transmission of KOH in the near infrared.

KOH samples 10^{-2} cm thick were grown between glass slides in an argon atmosphere. The transmission of these KOH-glass sandwiches was measured with a Perkin Elmer Model E-1 double-pass spectrometer. The dashed curve T of Fig. 1 is an inverted plot of the transmission data obtained. The transmission is that relative to an empty sandwich. It is obvious that there is no absorption in KOH that could lead to an explanation of the Mayer–El Naby anomaly.

B. Interference

The observation, shown in Fig. 1, that the spectral shape of the anomalous absorption remains unchanged as the magnitude of the effect builds up with increasing amounts of KOH on the surface is inconsistent with the supposition that the effect is caused by interference in KOH layers of increasing thickness. A KOH layer of unique thickness, but of increasing area of coverage, would require a reflectivity loss that oscillates with $h\nu$.

C. Surface roughness

Attack of a potassium surface by the chemical reaction (1) would be expected to roughen the metal surface. This will lead to light scattering[8-10] and a consequent loss in specular reflectivity. The spectral shape of this reflectivity loss depends somewhat on the scale of the surface roughness, but in general, it increases monotonically as $(h\nu)^4$ until an energy ~0.7 times the plasma frequency.[11] Since the plasma frequency of potassium corresponds to an energy of 3.8 eV, the spectrum of Fig. 1 cannot be ascribed to this mechanism. The early work[1] of Mayer and El Naby would also preclude this mechanism since they observed the anomaly to be essentially unchanged when the potassium surface became molten. (One would expect the surface roughness to be much smaller for a liquid interface.)

D. Plasmon absorption

Surface roughness also allows electromagnetic waves to couple to surface plasmons.[12] The loss in reflectivity caused by this interaction occurs, however, at 2.8 eV in potassium[4] (without a KOH coating). A recent theoretical study[13] has shown that as a dielectric layer is added the frequency of this absorption shifts to lower energy with increasing thickness of the layer. However, for thick layers the frequency approaches $\omega_p/(1+\epsilon)^{1/2}$, where ω_p is the bulk plasma frequency and ϵ is the (optical) dielectric constant. For KOH $\epsilon \sim 2$, so surface plasmon absorption could not occur below ~2 eV for potassium coated with KOH.

E. Scattering by KOH aggregates

A resonant loss of reflectivity could occur if the KOH formed large (~10 000-Å) clumps on the potassium surface. But one would then expect the spectral shape of such scattering to change continuously as the clumps grow in size, since scattering resonances are geometric in origin. (Even if one were to assume that KOH clumps had a unique size, the sharpness of the observed threshold at 0.6 eV could not be explained.[14] Moreover, a size distribution would be required to reproduce the monotonic behavior for $h\nu > 0.8$ eV so, in addition, one would have to require the size distribution to be independent of accumulated mass of KOH.)

F. Color centers in KOH

It is conceivable that KOH formed by reaction (1) at a potassium surface acquires a defect structure which would lead to color center absorption. Since excess K is available at the metal surface, the most probable defect would be OH^- vacancies with a trapped electron (for charge compensation), i.e., F centers. The energy of the F-band absorption in KOH (presuming that it exists) can be estimated from Ivy's law: $h\nu_F$ is a smooth function of the lattice constant. The molecular volume of KOH is intermediate between that of KF and KCl, for which $h\nu_F = 2.8$ and 2.3 eV, respectively. Therefore the F band in KOH should be near 2.5 eV. The validity of this argument has been tested[15] for the case of KCN, where the F band was found at 2.1 eV, compared to 2.0 eV for KBr. KCN has a slightly smaller lattice constant than KBr. (The forgoing mechanism would also be in difficulty from the standpoint of intensity since extraordinary concentrations of color centers would be required. Furthermore, the striking asymmetry of the anomaly would also be a problem.)

G. Surface states

The Mayer–El Naby anomaly is 10–20 times stronger than the fundamental interband absorption of potassium. The peak value of the latter[3,4] corresponds to an optical conductivity of $\sigma \sim 0.3 \times 10^{14}\ \text{sec}^{-1}$. The maximum anomalous absorption shown in Fig. 1 is about $4.5 \times 10^{14}\ \text{sec}^{-1}$. The integrated oscillator strength of this peak is about $f \sim 0.1$, a value derived on the basis that every atom within the penetration depth (~260 Å) of the light contributes equally. To attribute such an absorption to surface states would require an active site (having an oscillator strength $f \sim 1$) at each surface atom. Freshly cleaved surfaces of Si and Ge do exhibit[16] an absorption of comparable magnitude. It seems unlikely that a KOH-potassium interface, where surface states would necessarily overlap the conduction band continuum, could have a high density of sharp, occupied surface states and a complimentary narrow band of empty surface states (~0.8 eV higher). Although such hypotheses present serious difficulties, they cannot be ruled out completely.

H. Absorption by K particles in KOH

Meessen[17] has suggested that the Mayer–El Naby absorption arises from small (submicron) particles of potassium. In view of the Harms study these could be embedded in the KOH overlayer. For spherical particles the absorption resonance would occur[18] at $\omega_p/(1+2\epsilon)^{1/2}$, i.e., at ~1.7 eV. One can reduce this energy arbitrarily by assuming the particles are very flat spheroids parallel to the surface. This would seem to be a rather *ad hoc* and extreme assumption, and one that would be hard to reconcile with the invariant spectral shape shown in Fig. 1.

J. Impurity absorption in potassium

The surface reaction (1) could conceivably provide a source of H or O which, upon diffusion into the metal, might provide sites for optical excitation having the appropriate spectral shape and intensity. However H is insoluble in potassium.[19] A hydride, KH, could occur but it is not stable[20] at ambient pressures of 10^{-10} Torr. Solute oxygen can also be ruled out: Mayer and El Naby also measured the long-wavelength Drude absorption at 90 °K and found that it was consistent with the phonon resistivity of pure potassium (~2 μΩ cm) at that temperature. Since from Linde's rule[21] the expected residual resistivity of 1-at.% O in a monovalent metal is ~8 μΩ cm, the concentration of O in solid solution could only be 10^{-3} or less. The magnitude of the observed anomalous absorption is too large for such a small concentration, even if the O were to have an absorption (in K) of the required spectral shape and an oscillator strength near unity.

K. Unknown mechanism

If the Mayer–El Naby anomaly is to be attributed to an extrinsic mechanism, this one would seem to be more likely than the others discussed above. The structure of the hydrated layer produced by Harms has not been characterized nor has its thickness even been estimated. Under such circumstances it is useless to speculate further. One of the experiments proposed in Sec. IV should confirm any mechanism that could be attributable to the hydrated layer itself.

III. INTRINSIC MECHANISMS

From the foregoing discussion it seems that, at present, a satisfactory, extrinsic explanation of the Mayer–El Naby anomaly has yet to be found. It is possible that one may eventually be identified and shown experimentally to be the cause. Until such a time it is appropriate to examine the only alternative, namely, that the Mayer–El Naby anomaly arises from the properties of potassium metal itself. Such a postulate leads immediately to three tentative conclusions.

(i) Bulk potassium, although seemingly cubic, must be optically anisotropic. There must be an optic axis $\vec{a}$ such that the anomalous absorption occurs if the polarization vector $\vec{\epsilon}$ of the electromagnetic wave (in the metal) is parallel to $\vec{a}$, whereas if $\vec{\epsilon}$ is perpendicular to $\vec{a}$ absorption does not occur. $\vec{\epsilon}$ parallel to $\vec{a}$ must be the direction for absorption since, when the anomaly is not observed, it is absent for all $\vec{\epsilon}$ lying in a plane (the metal surface).

(ii) The optic axis $\vec{a}$ must be perpendicular to a glass-metal interface or a vacuum-metal interface. This assumption is required to account for the many negative observations.

(iii) Finally, the work of Harms requires that $\vec{a}$ is not perpendicular, and is possibly parallel, to a K-KOH surface. In other words an epitaxial deposit of KOH rotates $\vec{a}$ into the plane of the surface.

A theoretical model must be consistent with the foregoing properties and, in addition, must explain the unusual intensity and asymmetry of the absorption. Most early attempts to explain the Mayer–El Naby result failed to satisfy the properties given above. Only one model,[22] which assumes that potassium has a charge-density-wave (CDW) ground state, appears to be consistent with all of the requirements. In the remainder of this section we will elaborate on this observation.

A CDW introduces an additional periodic potential $V(\vec{r})$ into the one-electron Schrödinger equation for conduction electrons:

$$V(\vec{r}) = G\cos(\vec{Q}\cdot\vec{r}), \tag{2}$$

where $\vec{Q}$, the CDW wave vector, has a magnitude slightly larger than $2k_F$,[22,23] the diameter of the Fermi surface. This potential introduces new energy gaps of magnitude G into the one-electron energy spectrum $E(\vec{k})$. As a consequence there will arise a new optical absorption mechanism having a threshold at $h\nu = G$. The optical conductivity $\sigma(W)$, $W \equiv h\nu$, caused by electronic transitions from below to above the CDW gap has been calculated[23]:

$$\sigma(W) = \frac{G^2e^2Q}{8\pi\hbar W^2}\left(\frac{W-G}{W+G}\right)^{1/2}\left(1-\frac{W+G}{2\mu Q}\right)\cos^2\theta, \tag{3}$$

where $\mu \equiv \hbar^2Q/2m$ and θ is the angle between $\vec{Q}$ and the (electric) polarization vector $\vec{\epsilon}$ of the light. $\sigma(W) = 0$ for $W < G$. This result exhibits a uniaxial absorption, as required. The optic axis is coincident with the wave vector $\vec{Q}$. Multiple-$\vec{Q}$ CDW states are possible and have been observed in layer compounds.[24] However, for the case of potassium, the (apparent) need for a unique optic axis is consistent only with a single-$\vec{Q}$ CDW structure.

One of the remarkable properties of the theoretical $\sigma(W)$, given by Eq. (3), is that it explains the magnitude and shape of the Mayer–El Naby anomaly. This is shown in Fig. 2, where the Drude tail (caused by intraband conductivity) has been subtracted from the experimental points of Mayer and El Naby. The CDW energy gap was taken to be $G = 0.62$ eV and $\cos^2\theta = \frac{2}{3}$ for the theoretical curve. The data of Harms require a larger magnitude by about a factor of 2. A stronger absorption can arise theoretically as a result of collective corrections to the optical matrix element. Exchange and correlation effects lead to such an enhancement[25] when they are large enough to cause a CDW instability.

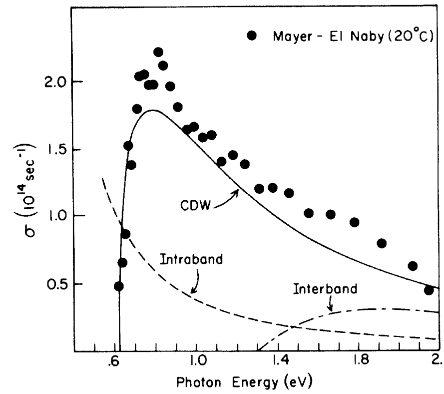

FIG. 2. Anomalous optical-absorption spectrum of potassium. The intraband conductivity, dashed curve, has been subtracted from the experimental data of Mayer and El Naby before the latter were plotted. The solid curve is the theoretical absorption of a CDW structure given by Eq. (3) of the text. The dot-dashed curve, starting at 1.3 eV is the fundamental interband absorption caused by the cubic-lattice periodic potential.

[The validity of Eq. (3) needs to be discussed. It was originally derived for optical transitions across an energy gap created by a spin-density wave (SDW). Hopfield[26] pointed out the matrix elements for transitions across (pure) SDW energy gaps have to be zero. This is true only when the periodic potential causing the energy gap arises exclusively from the conduction electrons. The periodic potential of a CDW, however, arises in part from the lattice modulation which necessrily accompanies the electronic modulation.[22] Consequently, Hopfield's remark does not apply. (Otherwise ordinary interband absorption could never occur.) A self-consistent theory[25] of the optical matrix elements leads to the conclusion that Eq. (3) is likely a slight underestimate, as observed above.]

A single-$\vec{Q}$ CDW structure is expected to cause a splitting of the conduction-electron spin resonance.[27] This effect has been reported[28] and confirmed as a g-factor splitting.[29] A gap of $G \sim 0.6$ eV is required to fit the observed splitting. If this phenomenon is employed to determine G, then the extraordinary agreement (within a factor of 2) between Eq. (3) and the observed anomaly can be achieved without an adjustable parameter. Energy threshold, asymmetric shape, magnitude, and uniaxial character are all accounted for.

Orientation of $\vec{Q}$ at various potassium interfaces remains to be discussed. A CDW in the electronic structure must be accompanied by a similar distortion of the positive-ion lattice in order to optimize microscopic charge neutrality.[22] Such ion displacements are equivalent to a static longitudinal phonon. To minimize the energy penalty of this distortion one expects $\vec{Q}$ to have a crystallographic direction for which a longitudinal phonon (having the same $|\vec{Q}|$) has the lowest frequency. For potassium this is a [110] direction.

When soft metals are evaporated on amorphous substrates (e.g., glass), the crystal grains have a preferred texture. The close-packed planes of the lattice lie parallel to the surface.[30] For potassium the normal to a glass-metal interface will be a [110] direction, i.e., one of the allowed directions for $\vec{Q}$. This means that the interfacial energy can be minimized by allowing the phase of the CDW to adjust so that either a maximum or minimum of electron density occurs at the boundary. Since the planes of constant electron density are perpendicular to $\vec{Q}$, optimization of the interfacial energy can occur only if $\vec{Q}$ is parallel to the [110] direction normal to the surface. It must be remembered that when light reflects from a metal surface, the polarization vector $\vec{\epsilon}$ (inside the metal) is parallel to the surface. Accordingly one does not expect a CDW optical anomaly in potassium to be visible at a glass-metal interface or at the vacuum-metal interface of an evaporated film. The CDW model explains therefore why Hodgson,[2] Smith,[3] and Palmer and Schnatterly[4] could not reporduce the Mayer–El Naby result.

Only Mayer and El Naby[1] and Harms[5] have measured the optical constants of potassium at a bulk-metal vacuum interface. Even if a clean bulk-metal vacuum interface had, say, a (100) orientation macroscopically, one would not expect to see the Mayer–El Naby absorption. Such a surface will quickly regrow into a washboard-like surface, with each facet having a (110)-type orientation, so as to minimize the surface energy. This explains why it is possible to not observe the anomaly on a bulk (and presumably polycrystalline) sample, as shown by curve *A* of Fig. 1.

The only *ad hoc* assumption that is required to provide a complete (and quantitative) explanation is that a KOH surface layer epitaxially puckers a potassium (110) surface so that $\vec{Q}$ can rotate into, say, the $[1\bar{1}0]$ direction. Or, alternatively, one can assume that a KOH layer stabilizes microscopic facets having other than (110)-type orientations. In either case $\cos^2\theta$, of Eq. (3), will acquire a nonzero average value and "turn on" the Mayer–El Naby anomaly.

IV. TWO CRITICAL EXPERIMENTS

The question whether the Mayer–El Naby anomaly is extrinsic or intrinsic is of considerable importance. An understanding of nature's simplest metal is at stake.[31] We now propose two experiments which may settle the issue. Of course it is of importance first to reproduce the work of Harms under conditions such that the amount of KOH formed on the surface can be measured and correlated with the optical anomaly. Then the following studies seem promising.

(a) Prepare a thin film of K (at least twice as thick as the hydrated layer needed to obtain curve *E* of Fig. 1) on a transparent substrate. Convert the entire specimen to "KOH" by admitting H_2O. Then measure the transmission coefficient of the completely hydrated sample. An absorption spectrum similar to Fig. 1 would prove that the anomaly is extrinsic, and is to be associated with electronic transitions in the hydrated layer (or on its surface).

(b) Boutry and Dormont[32] have shown by low-energy electron diffraction that a (100) K film can be epitaxially grown on a clean, cleaved KF substrate. Monin and Boutry[33] have confirmed that K films on optically plane glass are (110). Reflection specimens of both types should be prepared simultaneously and $\sigma(h\nu)$ measured. If both samples show a Mayer–El Naby anomaly, then the conditions of preparation would be at fault. If neither sample shows an anomaly, then the anomaly cannot be intrinsic since the [110] $\vec{Q}$ direction of a CDW would have to have a component parallel to the surface of the (100) specimen. If the (100) specimen were to show an anomaly when the (110) specimen did not, then the CDW mechanism would be definitely established.

ACKNOWLEDGMENTS

The authors are most grateful to Dr. Harms for making his results available to us in advance of publication, and to K. L. Kliewer for calling our attention to them. The KOH samples were kindly grown for us by G. Youchunas. We are indebted to a number of colleagues for helpful conversations about various aspects of this research.

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*Work supported by the NSF under Grant Nos. 41884 and GH 32001A1, and MRL Program No. GH 33574A3.

[1] H. Mayer and M. H. El Naby, Z. Phys. 174, 269 (1963); 174, 280 (1963); 174, 289 (1963).

[2] J. N. Hodgson, Phys. Lett. 7, 300 (1963).

[3] N. V. Smith, Phys. Rev. 183, 634 (1969).

[4] R. E. Palmer and S. E. Schnatterly, Phys. Rev. B 4, 2329 (1971).

[5] Peter Harms, dissertation (Technischen Universität Clausthal, 1972) (unpublished). The authors are very grateful to Dr. Harms for permission to reproduce his data, taken from Fig. 24 of his dissertation.

[6] M. Born and E. Wolf, *Principles of Optics* (Pergamon, London, 1959), Chap. XIII.

[7] R. A. Buchanan, J. Chem. Phys. 31, 870 (1959).

[8] E. Kröger and E. Kretschmann, Z. Phys. 237, 1 (1970).

[9] J. M. Elson and R. H. Ritchie, Phys. Rev. B 4, 4129 (1971).

[10] A. A. Maradudin and D. L. Mills, Phys. Rev. B 11, 1392 (1975).

[11] See Fig. 4 of Ref. 9.

[12] J. Bösenberg and H. Raether, Phys. Rev. Lett. 18, 397 (1967).

[13] D. L. Mills and A. A. Maradudin, Phys. Rev. B 12, 2943 (1975).

[14] Theoretical curves for dielectric spheres are given by Milton Kerker [*The Scattering of Light* (Academic, New York, 1969), p. 112].

[15] S. Susman, Ph.D. thesis (Illinois Institute of Technology, Chicago, Ill., 1963) (unpublished), Sec. IV, p. 27.

[16] G. Chiarotti, S. Nannarone, R. Pastore, and P. Chiaradia, Phys. Rev. B 4, 3398 (1971).

[17] A. Meessen, J. Phys. (Paris) 33, 371 (1972); see also J. P. Marton, Appl. Phys. Lett. 18, 140 (1971).

[18] R. Ruppin, Phys. Rev. B 11, 2871 (1974).

[19] R. M. Barrer, *Diffussion In and Through Solids* (Cambridge U.P., Cambridge, England, 1951), p. 146.

[20] S. Dushman, *Vacuum Technique*, 2nd. ed. (Wiley, New York, 1962), p. 768.

[21] F. J. Blatt, *Physics of Electronic Conduction in Solids* (McGraw-Hill, New York, 1968), p. 196.

[22] A. W. Overhauser, Phys. Rev. 167, 691 (1968).

[23] A. W. Overhauser, Phys. Rev. Lett. 13, 190 (1964). The right-hand side of Eq. (12) of this reference should be divided by 2. The error arose from using a complex vector potential, Eq. (7). When a real one is used Eq. (8) is smaller by 2 and Eq. (10) is smaller by 4. Equation (3) of the present paper is obtained from (the corrected) Eq. (12) of this reference by employing the relation $2nk/\lambda = 2\sigma/c$.

[24] J. A. Wilson, F. J. Di Salvo, and S. Mahajan, Adv. Phys. 24, 117 (1975).

[25] A. W. Overhauser, Phys. Rev. 156, 844 (1967).

[26] J. J. Hopfield, Phys. Rev. 139, A419 (1965).

[27] A. W. Overhauser and A. M. de Graaf, Phys. Rev. 168, 763 (1968).

[28] W. M. Walsh, Jr., L. W. Rupp, Jr., and P. H. Schmidt, Phys. Rev. 142, 414 (1966).

[29] G. L. Dunifer (private communication).

[30] R. C. Jaklevic and John Lambe, Phys. Rev. B 12, 4146 (1975).

[31] D. Gugan, Nature Phys. Sci. 235, 61 (1972).

[32] G. A. Boutry and H. Dormant, Phillips Tech. Rev. 30, 225 (1969).

[33] J. Monin and G. A. Boutry, Phys. Rev. B 9, 1309 (1974).