

NMR STUDY OF THE ELECTRONIC STRUCTURE OF SOLID AND LIQUID METALS

D. ZAMIR AND U. EL-HANANY

*Israel Atomic Energy Commission
Soreq Nuclear Research Center, Yavne, Israel*

ABSTRACT

NMR was used to study the effect of melting on the electronic structure of copper and aluminium. The Knight shift and spin-lattice relaxation time were measured as a function of temperature in the solid and in the liquid state. From these measurements the temperature dependence of $K(\alpha)$, the reciprocal enhancement factor of the Korringa relation, is obtained.

In the case of copper it is shown that the main temperature effect is indirectly through thermal expansion. It is shown that the conduction electrons density of states and spin density at the nucleus are strongly influenced by sd hybridization. Their temperature dependence is explained as due to the volume dependence of the hybridization.

In aluminium, in contrast to copper, the results of $K(\alpha)$ as a function of temperature cannot be explained as due to volume change, but rather a direct temperature effect.

The explanation is based on the strong mixing of states near the Brillouin zone. This mechanism should prevail only in polyvalent metals such as aluminium, in contrast to monovalent metals such as copper, where this effect can be neglected. The behaviour of other metals upon melting is discussed.

About twenty years ago, W. D. Knight discovered that the nmr line of a nucleus in a metal is shifted relative to its line in a nonmetal. This is the well-known Knight shift. This discovery made the nmr technique an important research tool in the study of the electronic structure of metals. The study of nmr in metals has become a very broad and active field.

We would like to discuss one problem in this field: the effect of melting on the electronic structure of metals. This is a problem to which nmr has made a significant contribution.

When a metal is heated, two major processes occur. The first is an increase in the lattice volume, which is gradual in the solid state and changes abruptly on reaching the melting point. The second is an increase in the amplitude of atomic vibrations, which can be looked upon as a gradual deviation from the order typical of the crystalline state, till a completely disordered state is reached at the melting point. We will discuss the effect of each of these two processes. In fact, a good test for any theory of electronic structure is its ability to explain the effect of a change of atomic volume and of order on

electronic properties. It seems that while the effect of volume can be calculated, the effect of order is less clear.

How can nmr contribute to this problem? As is well known, it is preferable to study electronic properties at the lowest possible temperatures. The reason is that at higher temperatures, phonons or any kind of atomic motion can mask the electronic properties. All the powerful techniques for the study of electronic structure, such as de-Hass van Alphen's, cyclotron resonance and so on, are typically low temperature techniques. These techniques obviously cannot be used to study our present problem. Melting, by its very nature, is a high temperature phenomenon, in the sense of its having many phonons and much atomic motion.

Now, instead of avoiding these perturbing phonons, one can use their interaction with the electrons to obtain information on the electrons. This is the basis of the techniques exploiting transport properties, such as electrical and thermal conductivity, which were the first and most common methods used in the study of liquid metals. However, transport properties are not sufficiently sensitive to probe changes in electronic properties such as density of states or wave function behaviour of the conduction electrons.

In contrast, in nmr the Knight shift and the spin-lattice relaxation depend explicitly on these electronic properties, and as regards the effect of phonons and atomic motion on the nmr properties, there are cases where these may either be neglected or readily eliminated.

We wish to discuss two specific metals which we have studied, namely copper and aluminium, which behave differently under change of temperature. We will discuss copper in greater detail and then compare it with aluminium and also with alkali metals.

The nmr technique exploits the interaction between the conduction electrons and the nuclei. One common feature of the metals just mentioned is that almost all the hyperfine interaction of the nucleus with the conduction electrons is due to contact hyperfine interaction. This interaction gives rise to the Knight shift

$$K_s = (8\pi/3)\Omega P_F \chi_p \quad (1)$$

where the Pauli susceptibility is $\chi_p = \frac{1}{2}(\hbar\gamma_e)^2 N(E_F)$ and $P_F = \langle |\psi(O)|^2 \rangle$ is the spin density at the nucleus, averaged over all the Fermi surface. This interaction also determines the spin-lattice relaxation time

$$\left(\frac{1}{T_1}\right)_s = \pi\kappa T \hbar^3 (\gamma_e \gamma_n)^2 \left[\frac{8\pi}{3} \Omega P_F \cdot N(E_F) \right]^2 \quad (2)$$

Here s stands for the s electrons, as only they contribute to the observed K and T_1 .

The density of states $N(E_F)$ and the quantity P_F are two electronic properties that characterize the metal band structure. As K and T_1 depend directly on these quantities, we expect nmr measurements in metals to be sensitive to changes in electronic structure.

Optical and transport properties change considerably upon melting and also show free-electron like characteristics in the liquid, whereas in the solid

they seem to be influenced strongly by band structure effects. Thus we expect nmr properties to change considerably too upon melting. Surprisingly however, the Knight shift in most of the metals changes only slightly. This apparent contradiction between nmr and transport properties has been challenged for a long time.

Several explanations have been suggested for the fact that Knight shift in many metals changes little on melting. One is that short range order is preserved in the liquid; however there is no convincing evidence for such an assumption. Another explanation is that the $N(E_F)$ in the solid and the liquid are both free-electron like—this also seems unlikely, at least in some metals such as lithium where the solid is not free-electron like, and nevertheless there is no change in K upon melting. We hope that our study of copper and aluminium throws some light on this problem.

We measured the Knight shift and spin-lattice relaxation of copper from room temperature up to the melting point, and in the liquid state up to 1250°C^1 . Special attention was paid to achieving high accuracy in the measurements, a matter of great importance, as will be seen later on.

We have confirmed that the effects measured come only from the conduction electrons. This is one of the difficulties mentioned earlier of working at high temperatures. As regards the Knight shift, which results from the *static* part of the hyperfine interaction, there can be no ambiguity, but T_1 can be very sensitive to atomic motion such as lattice vibration or diffusion. Especially in copper, which has a quadrupole moment, the effect of atomic motion on T_1 might be significant. Fortunately, copper has two isotopes with different quadrupole moments. Comparing the T_1 of the two isotopes, it can easily be shown that the effect of atomic motion is negligible, and therefore the measured spin-lattice relaxation in copper may be taken to result from magnetic hyperfine interaction with the conduction electrons¹.

The dependence of any phenomenon on temperature originates from two effects—the *direct* and the *indirect*. For example, the dependence of the Knight shift on temperature will be:

$$\left(\frac{\partial K}{\partial T}\right)_P = \left(\frac{\partial K}{\partial T}\right)_V + \left(\frac{\partial K}{\partial V}\right)_T \times \left(\frac{\partial V}{\partial T}\right)_P \quad (3)$$

The best way to separate these two effects is to measure, in addition to the *temperature* dependence of K , also its *pressure* dependence (keeping the temperature constant). From the latter, we obtain only the effect of volume, which can be subtracted from the overall temperature dependence to give the direct effect of temperature.

Some years ago, Benedek and Kushida measured the Knight shift of copper as a function of pressure². Although the range of volume change was quite small, due to the small compressibility of copper, one can show, by comparing their results with our measurements, that the explicit temperature dependence of K in copper can be neglected. Therefore, from now on we shall present our data for copper as a function of volume.

What is the mechanism which causes the Knight shift to change with volume? Let us look at the Knight shift formula again: it contains two quantities $N(E_F)$ and P_F .

Assuming free electron behaviour, that is, no band structure effect, it can be easily shown that K is proportional to $\Omega^{-\frac{1}{3}}$, and therefore should *decrease* with increasing volume, which is obviously not the behaviour we obtain experimentally. In order to understand what happens, we would like to obtain the behaviour of $N(E_F)$ and P_F *separately* as a function of volume.

The way to differentiate between them, is to use the relation between the two measured quantities K and T_1 known as the Korringa relation.³ Assuming no electron-electron interaction it relates T_1 and K as follows:

$$K^2 T_1 T = (\hbar/4\pi\kappa) (\gamma_e/\gamma_n)^2 \equiv \eta \quad (4)$$

However, this relation, in the above form, is almost never obeyed. This is due to electron-electron interaction, which is not taken into account in the derivation of the relation. The electron-electron interaction enhances the independent electron susceptibility, so that the Pauli susceptibility becomes

$$\chi_p = \chi_p^0/(1 - \alpha) \quad (5)$$

and the Knight shift, which is proportional to χ_p , is enhanced similarly.

When electron-electron interaction can be represented by an effective potential $V(q)$, where q is the momentum transfer between the interacting electrons, then the enhancement parameter is $\alpha = V(0) N(E_F)$. The spin-lattice relaxation rate is also expected to be enhanced, but, as shown by Moriya⁴, its enhancement is *weaker* than that of the Knight shift

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)^0 \langle [1 - F(q) V(q)/V(0)]^{-2} \rangle \quad (6)$$

where $F(q)$ is the static response function of noninteracting electrons, and the outer brackets indicate averaging over all the pairs of states on the Fermi surface having a momentum difference q . As K and T_1 are enhanced to different extents, the Korringa relation will have a new form

$$K^2 T_1 T = \eta/K(\alpha) \quad (7)$$

where $K(\alpha)$ is a complicated function of α .

There are several calculations of the dependence of $K(\alpha)$ on α . We cannot enter into the details of these calculations, but we can show through them that the results of our present study are not sensitive to the choice of the model for the electron-electron interaction.

We chose to use the recent calculations of Shaw and Warren⁵, represented by graph B in Figure 1. It has been shown that the enhancement of the Korringa relation in the alkali metals is accounted for by this $K(\alpha)$ ⁵. The main difference between the various calculations of $K(\alpha)$ is the assumption about the range of the electron-electron interaction. For a long-range interaction, for instance, it can be shown that the relaxation rate is *not enhanced* and as a result $K(\alpha) = (1 - \alpha)^2$. Graph C represents this behaviour. Graph A on the other hand, represents the other extreme assumption of a very short-range interaction, namely a δ -function⁶. The need for a relation $K(\alpha)$ will be seen later, when we use it to get important information on the electronic density of states.

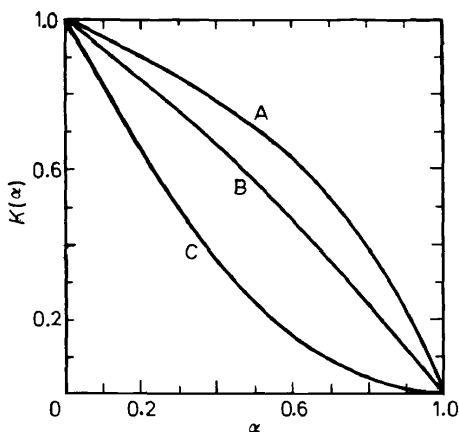


Figure 1. The reciprocal enhancement factor of the Korringa relation $K(\alpha)$, as against the enhancement parameter. The different calculations were made assuming for the interaction (A) δ -like behaviour⁶, (B) short but finite range,⁵ (C) long range.

As to terminology, we use the term 'independent electron gas', in the sense of electrons *without* electron-electron interaction, and we use the word 'free' for electrons free of the atomic potential, that is free of what is called the band structure effect.

So far we have included only the effect of electron-electron interaction on the Knight shift and T_1 , and we got the enhanced Korringa constant $K(\alpha)$. So our electrons are not 'independent' any more, but still 'free', (a quite familiar situation!).

But of course we do have to include the effect of the lattice, or the band structure.

The band-structure effect can be included using the method of Silverstein⁷, which gives

$$\alpha = \alpha_f \left(\frac{m^*}{m} \right) \quad (8)$$

Here f stands for free electron model, and $(m^*/m) \equiv N(E_F)/N_f(E_F)$ is the band effective mass ratio. The expression for the spin susceptibility, taking into account both the electron-electron interaction and the band-structure effect is

$$\chi_p = \frac{m^*/m}{1 - \alpha_f(m^*/m)} \chi_f^0 \quad (9)$$

Let us see now how, by using the above relation, we can get the separate dependence of m^* and P_F on volume. From the dependence of K and T_1 on volume, we obtain, using the modified Korringa relation, the dependence of $K(\alpha)$ on volume. This dependence, in the case of copper metal, is given in Figure 2 which actually summarizes the measurements of both the K and T_1 ¹. It is seen that $K(\alpha)$ changes considerably over the present volume and temperature ranges. The next step is to use the dependence of $K(\alpha)$ on α ,

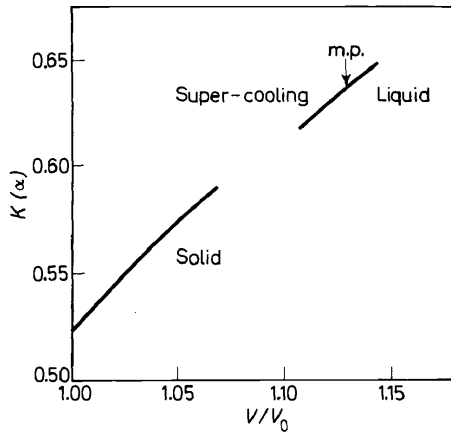


Figure 2. The reciprocal enhancement factor of the Korringa relation, $K(\alpha)$, in copper metal, as function of volume.¹

as calculated by Shaw and Warren, and to obtain the volume dependence of α . This volume dependence of α may be brought about by both α_f and m^* . It can be shown that the volume dependence of α_f is very small, relative to that of α^8 . Thus we assume that the whole volume dependence of α is caused

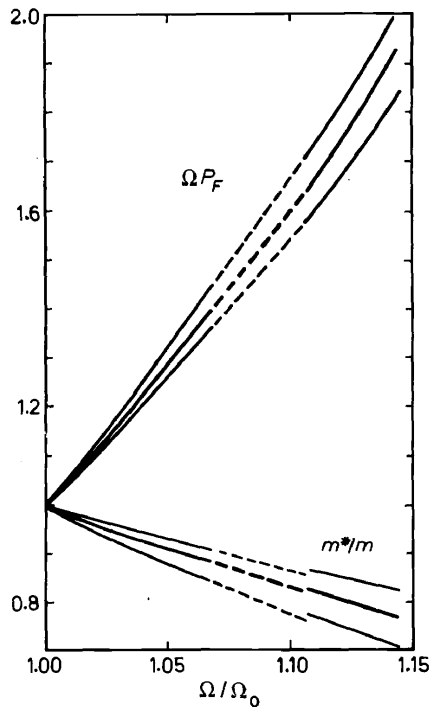


Figure 3. m^*/m and ΩP_F as against volume, derived from the experimental data of K and T_1 . Both quantities are presented as relative to their room temperature values.

by m^*/m . Using this dependence and the Knight shift dependence on volume, we get the second dependence, namely that of P_F , on volume.

Both these dependences are plotted in *Figure 3*. The upper and lower graphs in each case are obtained by assuming the two extreme cases of interaction, a δ -function and a long-range electron-electron interaction. The main features of these graphs are

1. A strong volume dependence of P_F .
2. P_F changes smoothly through melting; in fact, its behaviour in the liquid is *almost an extrapolation* from the solid.
3. A weaker volume dependence of m^* , with a discontinuity of about 2 per cent in the transition from the solid to the liquid.

This is an interesting result, as it shows that the main effect of melting is due to the change in volume.

The destruction of order seems to have no effect on P_F , and only a slight effect on the density of states. In order to understand the reason for this, we have to enter briefly into the details of the electronic structure of copper.

The features of the band structure of copper are well-known, being a metal widely studied, both theoretically and experimentally. Copper has an atomic configuration $3d^{10}4s$. The electronic band structure in the solid state is governed by the $3d$ states. These states do not behave like unperturbed atomic core states; on the contrary, they are quite strongly perturbed by the lattice potential. Thus, the d states form a narrow band, the energy of which falls just about in the middle of the broad s band. The interaction between the d and s electrons causes the phenomenon of hybridization, which is described schematically in *Figure 4*. The broken lines depict the broad s band and the narrow d band, with no interaction between the two. As a result of the interaction the bands take the form given by the full line, as can be shown by a simple calculation.

The system of a broad free electron band and a narrow d band can be

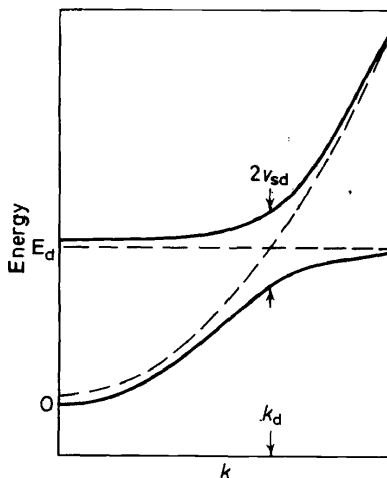


Figure 4. Hybridization between a free-electron band and a d -level, (the dashed lines), for the case $V_{sd} = \frac{1}{4} E_d$.

described in the following manner. Both the free electron band $\hbar^2 k^2/2m$ and the d level E_d are described by a 2×2 model Hamiltonian

$$H = \begin{vmatrix} \frac{\hbar^2 k^2}{2m} & V_{sd} \\ V_{ds}^* & E_d \end{vmatrix} \quad (10)$$

where V_{sd} is the hybridization matrix element. To get the energy as a function of K , we solve the secular equation and get

$$E = \frac{1}{2} \left\{ E_d + \frac{\hbar^2 k^2}{2m} \pm \left[\left(E_d - \frac{\hbar^2 k^2}{2m} \right)^2 + 4V_{sd}^2 \right]^{\frac{1}{2}} \right\}$$

(which is described by the solid line in Figure 4 for the special case of $V_{sd} = E_d/4$).

As a result of the hybridization there is a splitting of the two low mixed bands. The splitting is given by $2V_{sd}$ at the intersection point. The other effect is that far from the intersection point, namely when $\hbar^2 K^2/2m - E_d \gg V_{sd}$, there is a *second order shift* of the free electron energy

$$\delta E \sim V_{sd}^2 / [\hbar^2 k^2/2m - E_d]$$

Such a shift will influence the density of states at the Fermi level. Let us recall that the density of states at the Fermi level is defined as

$$N(E_F) = \frac{1}{(2\pi)^3} \int \frac{d^2 K}{(dE/d(k))_{E_F}} \quad (11)$$

where the integration is over the whole Fermi surface. Then, using an approximation of a Fermi sphere, and the energy shift due to hybridization, one gets¹

$$\frac{m^*}{m} \sim \frac{S}{S_f} \frac{1}{1 - [V_{sd}/(E_F - E_d)]^2} \quad (12)$$

where S is the actual area of the Fermi surface and S_f is its free-electron equivalent.

In order to obtain the volume dependence of m^* we have to know S , $E_F - E_d$ and V_{sd} as a function of volume. The dependence of $E_F - E_d$ on volume is obtained from optical measurements as a function of temperature⁹ and pressure.¹⁰ What about the dependence of V_{sd} on volume? Fortunately, there are self-consistent calculations performed by Jacobs¹¹ and the volume dependence obtained in this way has been confirmed by an independent estimate based on the measurement of a direct optical transition as a function of temperature.

The dependence of hybridization parameter V_{sd} on volume is the result of special features of the d wave function; these wave functions are distorted in the solid relative to their shape in the free atom. The amount of distortion is sensitive to the distances between the atoms, or in other words, to the

volume. The amount of distortion affects the s-d interaction and thus the hybridization is sensitive to volume.

In Figure 5 the dashed line represents the volume dependence of m^*/m in the solid and liquid state, as derived using the procedure described. We assume that upon melting order is completely destroyed. As a result, the structure

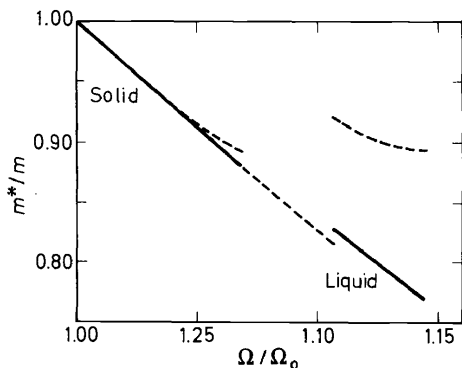


Figure 5. m^*/m as against volume (relative to room temperature value). The solid line is the experimentally derived value, whereas the dashed line is theoretical.

of the Fermi surface, which is a reflection of the order, is smeared out. In the case of copper the eight necks that touch the Brillouin zone disappear and the Fermi surface becomes a sphere. In the solid, the states on the eight faces of these necks do not contribute to the S appearing in the calculation of the density of states; but in the liquid we have to add the area of these necks to our calculation, and by doing so we obtain an increase in the calculated density of states. The solid line in Figure 5, on the other hand, represents m^*/m as derived from our measurements. One can see that in the solid state the agreement of calculations with experiment is very good, but in the liquid there is a considerable difference. We think that the reason for this discrepancy is that in calculating m^*/m for the solid phase, we neglected the contributions to the density of states coming from singularities in the energy. These singularities arise from the actual contact of the Fermi surface with the Brillouin zone boundaries. The contributions are positive and equal to a few per cent of the total density of states¹². Upon melting, order is destroyed and the singularities disappear together with the Brillouin zone and necks. So the loss of order has two effects that seem almost to cancel each other.

To sum up, in the solid and the liquid we can explain the behaviour of the density of states as mainly a volume effect, through the effect of hybridization. On melting, in addition to the volume effect, there is a small change in m^* resulting from loss of order.

We would like now to discuss the behaviour of P_F . Two things characterize this behaviour—strong volume dependence, and smooth extrapolation of P_F vs volume curve from the solid into the liquid state. Just from a simple qualitative consideration we can explain this behaviour as follows: in copper the only contribution to P_F is from electrons which are on the Fermi level and have s-type wave functions. The hybridization V_{sd} causes a large amount

of the Fermi level wave function to be of the d type, which does not contribute to P_F . The amount of d or non-s character is proportional to V_{sd} . As the volume increases, V_{sd} decreases, the amount of non-s character decreases and hence P_F increases with volume.

To calculate P_F we have to know the wave function on the Fermi level. A few attempts at such a calculation have been made for copper, but none of them aimed at obtaining the volume dependence of P_F . The simplest approximation for P_F is made by assuming a single OPW behaviour of the Fermi electrons. However, though this method is quite successful for calculating P_F of many metals, it gives for copper a value of P_F much larger than that derived from experiment¹³. Moreover, the OPW method does not give a volume dependence of P_F . While incorporating the hybridization effect by way of renormalizing the OPW-wave function (taking into account the d-character mixed into it) the volume dependence achieved is only one fifth from that derived from experiment¹.

Using a KKR method of calculation, Davis *et al.*¹⁴ got a value of P_F much closer to the experimental value. In this method the many-electron effects, namely exchange and correlation, are taken into account. These effects seem to modify strongly the wave functions and P_F in copper, due to hybridization causing mixture of 3d-character into the conduction wave function. These correlation effects might also be the reason for large dependence of P_F on volume. In Figure 6 we draw our experimental values of P_F versus the

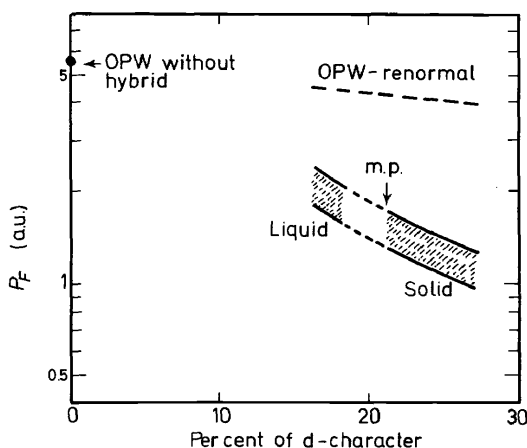


Figure 6. P_F as against d character of the Fermi electrons: $[V_{sd}/(E_F - E_d)]^2$. The shaded area is experimentally derived, whereas the dashed line is calculated by the OPW method. The uncertainty in the absolute value of P_F is due to large inaccuracy in estimating core-polarization contribution.

percentage of d wave function in the total wave function on the Fermi level. This percentage is calculated using the effect of volume on V_{sd} , E_F , E_d . Extrapolation of the curve to zero per cent d shows that P_F reaches its value calculated by the simple OPW method, without hybridization. It is reasonable to conclude then that hybridization not only reduces the value of P_F but also brings about its strong volume dependence.

As to the effect of melting, the dependence of P_F on volume in the liquid is an extrapolation of that in the solid. The only effect of melting on P_F is that of the accompanying volume change. This picture agrees well with the conclusion that the copper band structure is dominated by hybridization, which is very weakly influenced by order.

We have performed the same kind of K and T_1 measurements on aluminium up to the melting point and in the liquid state¹⁵. We analyzed the results in the same manner, first eliminating all the effects on T_1 that are not of an electronic nature. Then we attempted to determine the relative contributions of the two kinds of temperature effects—the direct and the indirect—through thermal expansion. Fortunately, Kushida and Murphy¹⁶ have measured quite recently the effect of pressure on aluminium Knight shift; using their results and our own, we could determine both these quantities.

Contrary to the results in copper, in aluminium we found a large explicit temperature dependence of the Knight shift. $(\partial K/\partial T)_V$ has a large positive value, whereas $(\partial K/\partial V)_T$ is negative. Thus, in aluminium the effect of raising the temperature is entirely different from that in copper. It not only changes the Knight shift by expanding the lattice but also, and quite significantly, influences K by destroying the order.

What are the individual behaviours of m^* and P_F in aluminium? Using the modified Korringa relation, we get from our measurements the temperature dependence of $K(\alpha)$. It is given in *Figure 7* versus atomic value, keeping the temperature an implicit parameter. $K(\alpha)$ has a considerable temperature dependence in the solid, whereas it is almost independent of temperature in the liquid state. We can see that this behaviour is different from that of copper. Following the same procedure as in copper, we get a strong dependence on volume of both m^* and P_F in the solid, while in the liquid they are almost volume independent. This is a surprising result for aluminium. Being almost a free metal, with m^* close to unity, we do not expect to get such volume dependence of these quantities, or not the twenty per cent rise in m^* we obtained. There is no mechanism related to band structure, like the hybridization in copper, that we can invoke in the case of aluminium.

There must be something wrong in the method of deriving m^* and P_F from $K(\alpha)$ in the case of aluminium. It seems that the existing calculations

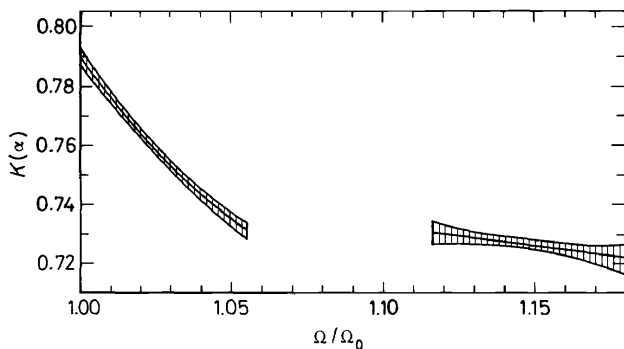


Figure 7. $K(\alpha)$ in aluminium metal, as function of volume¹⁵. Temperature is an implicit parameter.

of $K(\alpha)$ which are correct for monovalent metals, like copper, are not valid for aluminium, which is a trivalent metal.

How can this feature of being a trivalent metal affect the above calculations? Deriving the $K(\alpha)$ we assume a spherical Fermi surface, which is a good assumption in the case of most of the monovalent metals. One result of this assumption is that the electron-electron interaction is not dependent on the momentum of each electron taking part in the interaction, but rather on the momentum transfer. However, aluminium, being a trivalent metal, occupies three Brillouin zones and its Fermi surface cuts the boundary between the second and third Brillouin zones. As a result there is a strong mixing between states whose momenta differ by a reciprocal lattice vector. It can be shown that because of this mixing the formula for $K(\alpha)$ as given for a spherical Fermi surface is not correct, but rather the effective $K(\alpha)$ has a higher value than in the monovalent case.

In the liquid, as a result of destroying order, there is no Brillouin zone to speak of; the above effect which is of structural character disappears and one gets a reduction of $K(\alpha)$ to a value close to the free-electronic case. We can see in *Figure 7* that this is really the behaviour of $K(\alpha)$ in aluminium.

The effect of the rising temperature in the solid is to smear off the structural

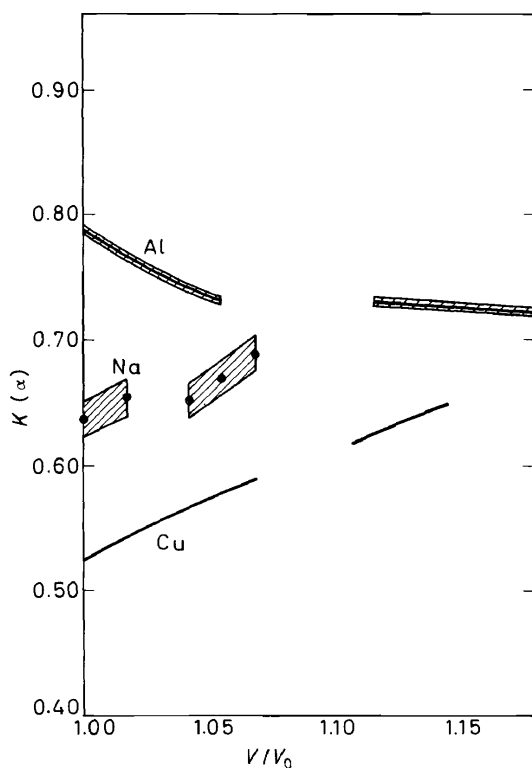


Figure 8. $K(\alpha)$ as against volume for copper¹, aluminium¹⁵ and sodium.¹⁷ The uncertainty in $K(\alpha)$ of sodium is due to inaccuracies in the data for K and T_1 .

effects and thus reduce $K(\alpha)$ gradually. This is qualitatively in accordance with the behaviour in aluminium.

In the last figure, *Figure 8*, we compare the behaviour of three metals—copper, aluminium and sodium. We chose to compare between $K(\alpha)$ as against the volume, because this quantity is in some way representative of the different effects of temperature on the electronic structure of the metal. In copper it was shown that the change in $K(\alpha)$ is due to the effect of volume change on the band structure parameters. In aluminium it seems that it is the direct temperature effect which induces the change in $K(\alpha)$ in the solid. In sodium, being a monovalent free-electron metal we expect weak dependence of $K(\alpha)$ on both volume and temperature. Unfortunately, the accuracy in the available results¹⁷ are not good enough to exemplify this point.

One can conclude that sufficiently accurate data of T_1 and K as functions of temperature can be used to learn about the effects of temperature on the density of states and the spin density P_F . We hope that our discussion has thrown some light on the problem of the effect of melting on the Knight shift, and also on the electronic structure of metals.

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