to a crystallographic phase change.

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Magnetic Breakdown and Dingle Temperature in Zinc Alloys

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Measurements of magnetic breakdown in dilute alloys of zinc show that the breakdown field between the second-zone monster and the third-zone needles increases linearly with the Dingle temperature with the same scaling factor for all alloys measured. A WKB calculation yields a general expression for breakdown in the presence of scattering which is in good agreement with experimental observations.

A study of the Dingle temperature in the de Haas–van Alphen (dHvA) effect is one of the most effective ways of investigating conduction-electron scattering in metals and alloys. The measured Dingle temperature X for a particular orbit is a direct measure of the average scattering around that orbit.[1] In some metals, however, such as zinc and its alloys, measurement of X is hampered by the occurrence of magnetic breakdown (MB) which permits electrons arriving at a zone boundary to tunnel between different sheets of the Fermi surface. In zinc the two relevant sheets are the second-zone-monster surface and the third-zone needles. This tunneling, characterized by a breakdown field H_0 and a corresponding transition probability $\exp(-H_0/H)$,[2] reduces the dHvA amplitude and, unless corrections are made, yields spurious values for X. On the other hand, in spite of the evident importance of the problem, there has been very little attempt to investigate magnetic breakdown occurring concurrently with strong scattering. Theoretical treatments[3] have only considered the interaction between the magnetic field and the lattice potential, so that the breakdown field is given purely in terms of band parameters. This approach appears to be valid in pure metals, where the scattering is weak and dominated by dislocations, but there is no justification for it in alloys, nor any experimental evidence to support it.[4]

We have therefore made and analyzed measurements of the breakdown field and the Dingle temperature for the needle surface in several alloys of zinc containing up to 210 ppm Mn and 165 ppm Cr. These alloys are so dilute that any large change in H_0 cannot be accounted for by change in the band structure[4] since this is almost the same as for pure zinc. The results show unequivocally that, far from being independent of scattering, magnetic breakdown is very strongly affected by it and that the breakdown field is related to the Dingle temperature in a very simple way.

Both H_0 and X were determined from the *absolute* amplitude of dHvA oscillations by a torque method already used by two of the authors for pure zinc.[5] The use of absolute amplitudes is necessary since, as explained in Ref. 5, relative amplitudes can only be relied on to give a lower

bound to H_0. To avoid any change of scattering from the magnetic field, data were analyzed only at 4.2 K in the field range 0 to 9 kG,[6] while the magnetic field was aligned within 15° of the c axis. Only the fundamental oscillation of the torque, $\Gamma_0(H)$, was observed and an expression for this is given by the Lifschitz-Kosevich[7] expression for the free energy of conduction electrons in a magnetic field modified for the presence of MB.

Falicov and Stachowiak[8] allow directly for leakage out of the orbit while preserving the phase coherence of the electron wave function during tunneling and around the orbit. This gives

$$\beta(H,H_0)=\beta_0\exp\left[\frac{-2\pi^2k_Bm^*c}{e\hbar}\frac{X}{H}\right], \quad (1)$$

where $\beta(H,H_0)$ is related to $\Gamma_0(H)$ by

$$\beta(H,H_0)=\Gamma_0(H)\left(\frac{\sinh(2\pi^2k_BTm^*c/e\hbar H)}{TH^{1/2}}\right)\times[1-\exp(-H_0/H)]^{-3/2}. \quad (2)$$

β_0, the infinite-field intercept, contains the usual curvature factor for the extremal area (defined exactly for the needles in Ref. 5) and includes both the spin-splitting factor and the volume of the specimen (~ 0.25 cm^3). Here it is *calculated* from a knowledge of the shape of the needle surface. Even for the most concentrated alloys it has a value within 7% of pure zinc.[5,9] X is the Dingle temperature and the remaining quantities in (2) have their usual meaning. An alternative method was suggested by Condon[4] in which breakdown is regarded simply as a scattering process so that a term

$$\frac{e\hbar H}{2\pi^2k_Bm^*c}\left[\tfrac{3}{2}\exp\left(\frac{-H_0}{H}\right)\right],$$

is added to X. With their more concentrated alloys, Higgins and Marcus[4] were unable to distinguish experimentally between these two approaches but preferred the latter since the data could then be fitted with the same H_0 as for pure zinc. Our data however cannot be described at all by the Condon expression whereas it fits the Falicov and Stachowiak model very well. We therefore conclude that Eq. (1) is correct and use it to determine X and H_0 graphically as illustrated in Fig. 1.

Figure 2 summarizes the results for *Zn*Mn and *Zn*Cr. We see that both X and H_0 increase rapidly and linearly with concentration, though at slightly different rates in the two systems. However, the ratio

$$\alpha=(\partial H_0/\partial x)/(\partial X/\partial x),$$

(where x is the solute concentration) is a constant for all our alloys and has a value of about 0.35 kG/°K. This very striking *empirical* relation would seem to hold for all zinc alloys so far measured, as is shown in Table I, even though the individual concentration dependences of X

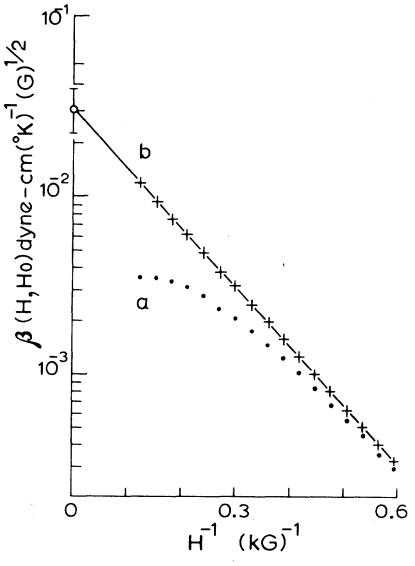

FIG. 1. Graphical determination of H_0 and X for zinc with 135-ppm manganese at 4.2°K. The magnetic field lies at 15° to the c axis. (a) Experimental data uncorrected for breakdown, i.e., $\beta(H,H_0)$ with $H_0=\infty$. (b) H_0 chosen as 4.8 kG which causes the plot to be linear and to take the calculated infinite-field intercept, β_0, shown on the ordinate with error bar. The slope yields X.

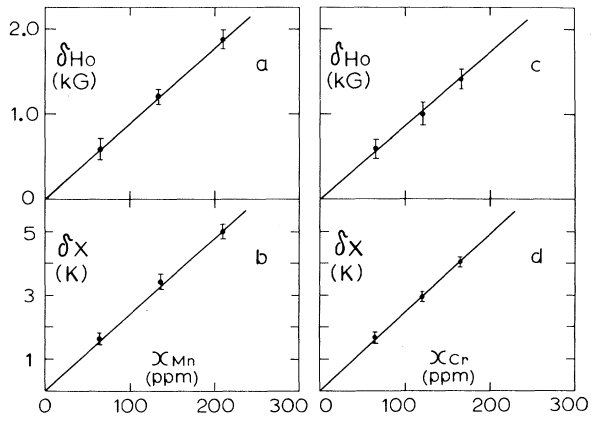

FIG. 2. The behavior of $\delta H_0=H_0^{\text{alloy}}-H_0^{\text{zinc}}$ and $\delta X=X^{\text{alloy}}-X^{\text{zinc}}$ with solute concentration. (a),(b) zinc manganese; (c),(d) zinc chromium. $H_0^{\text{zinc}}=3.5\pm0.3$ kG. X^{zinc} is taken from the value in the alloys extrapolated to zero concentration (see also Ref. 12).

TABLE I. A summary of the breakdown field and Dingle temperature in zinc alloys showing the constancy of α.

Alloy	$\partial H_0/\partial x$ (kG/at.%)	$\partial X/\partial x$ (°K/at.%)	α (kG/°K)
ZnMn	90	248	0.36 ± 0.06
ZnCr	88	240	0.36 ± 0.06
ZnAl [a]	23	45	0.50 ± 0.25 [c]
ZnCu [a]	11	22	0.50 ± 0.25
ZnHg [b]	2.2	5	0.44 ± 0.20
ZnCd [b]			

[a] Ref. 4, interpreted on the basis of Ref. 8.
[b] W. L. Gordon, private communication.
[c] Ref. 11.

and H_0 vary over 2 orders of magnitude.

It is therefore clear that conventional analyses of breakdown are only valid in the limit of weak scattering and that strong scattering inhibits the tunneling process. Qualitatively one can understand this by visualizing the two processes as in direct competition, so that an electron arriving at a zone boundary can either be scattered by the impurities or can tunnel to a neighboring sheet of the Fermi surface. Thus the effective tunneling probability is reduced. We have made a quantitative analysis of this effect by following the usual WKB calculations, starting with a Hamiltonian which includes impurities through a self-energy Σ whose imaginary part gives the scattering. The details of the calculation will be presented elsewhere.[9] Here we give only the result, using a $\vec{k}\cdot\vec{p}$ Hamiltonian whose validity for the needles in zinc is well established.[10]

If we follow the usual procedure of evaluating the tunneling between the points of closest approach[3] of the two surfaces and also assume that the electron scattering is completely isotropic, then the tunneling probability becomes:

$$P = \exp\left\{-\frac{H_{00} + \alpha' \delta X}{H}\right\}, \qquad (3)$$

where $H_{00} = (\pi \Delta^2 c/4\hbar e v_x v_y)$, the conventional expression for the breakdown field, $\alpha' = (2\pi c k_B/\hbar e v_x v_y)$, and $\delta X = (X^{\text{alloy}} - X^{\text{zinc}}) = \mathrm{Im}(\Sigma)/\pi k_B$. Δ is the band gap, while v_x, v_y are the components of the free-electron velocity perpendicular and parallel to the zone face where breakdown occurs. Equation (3) gives a form for the tunneling in agreement with the two features of the experimental results; the breakdown field increases linearly with the Dingle temperature with a scaling factor which is a property of the host, *not* the impurity.[11] Substituting the band parameters for zinc we find $\alpha' \simeq 0.20$ kG/°K, rather lower than the experimental value. However, agreement may be substantially improved if we adopt a suggestion of Chambers[13] and carry out the tunneling integration over a "free-electron" path between the two surfaces rather than the line of closest approach. Furthermore, preliminary analysis indicated that this approach may also explain the angular dependence of H_0 for zinc alloys.[9] We are at present pursuing this line of investigation and are also extending our experimental investigations to magnesium alloys.

In conclusion, measurements of magnetic breakdown in dilute alloys of zinc have shown that the tunneling probability is sensitive to electron scattering. A WKB calculation has yielded a general expression relating the breakdown field and the Dingle temperature in general agreement with the experimental observations.

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not. We have verified this experimentally (Ref. 9) in several samples of pure zinc and it is also consistent with our theoretical analysis. Dislocations increase X through "dephasing" of the electron wave function [A. B. Pippard, Proc. Roy. Soc., Ser. A 287, 165 (1965)] while H_0 only changes with direct scattering. We thus compare H_0 with the *change* in X due to the solute.

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New Interpretation of the Soft-X-Ray Absorption Spectra of Several Alkali Halides*

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Theoretical calculations have thus far been used to interpret the soft-x-ray spectra of several alkali halides in terms of band structures alone, excluding the possibility that core excitons are formed below the band edge. By independently determining the threshold for band transitions from x-ray photoemission spectroscopy and optical-gap data, we conclude that these spectra are in fact almost entirely excitonic in nature.

Absorption spectra are well known to contain valuable information about the excited states of a crystal. X-ray spectra are particularly convenient for this purpose since electrons are excited from core states which are flat and thus introduce no structure. By assuming constant transition matrix elements over the range of interest, one expects the observed structure to correlate directly with structure in the density of states (DOS) of the conduction bands. Because of the difficulty of computing absolute transition energies, a common practice has been to freely move the DOS on the energy axis until a reasonable correspondence between theoretical and experimental peaks and valleys is obtained. This approach has led to the interpretation of the soft-x-ray spectra of various alkali halides[1-3] in terms of band structures alone, dismissing the possibility that excitons are formed below the band edge. More recent theoretical work[4,5] has arrived at similar conclusions by using calculated transition energies instead of freely aligning spectra.

Such an interpretation of soft-x-ray spectra may be tested directly by making use of additional experimental information from x-ray photoemission spectroscopy (XPS) and optical-gap data in order to pin down the position of the conduction-band edge with respect to the core levels.[6] In this Letter we will use this powerful technique to show that several soft-x-ray spectra must be reinterpreted in a way that contradicts most of the previous work on the subject.

We first concentrate on the lithium halides LiF, LiCl, LiBr, and LiI. Haensel, Kunz, and Sonntag[7] first measured their Li^+ K spectra (Fig. 1) and suggested that the prominent peak in each spectrum at about 60–62 eV is probably an exciton while the remaining structure may be transitions to p-like band states. No band edges were identified.

The same spectra were measured and interpreted shortly thereafter by Brown *et al.*[1] These authors, and subsequently Kunz and Lipari,[2] performed Hartree-Fock band calculations for LiCl and LiBr and computed the DOS of the conduction bands. By freely shifting the DOS on the energy axis, they aligned theoretical and experimental peaks and valleys and concluded that the observed spectra are entirely due to transitions to conduction-band states with no excitons being formed. By analogy with LiCl and LiBr, Kunz, Devreese, and Collins[8] assumed that the band threshold for LiF lies at 60.5 eV and proceeded to identify a two-electron excitation (core-to-band plus a valence exciton) at about 70 eV. More recently, band calculations for LiF were reported by Menzel *et al.*[4] who used Slater exchange and by Kunz, Mickish, and Collins[5] who used nonlocal Fock exchange. In both cases, the observed structure was identified with similar structure in the computed interband spectra.[9] Both Refs. 4 and 5 predicted a long weak tail to the left of the main